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Evaluation of Yttrium Stabilized Zirconium Thin Films with Secondary Ion Mass Spectrometry

By

Jeff Serfass

Submitted in partial fulfillment of the requirements for the degree

Master of Science

Department of Physics

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Seton Hall University
College of Arts and Sciences
Department of Physics

Approval for Successful Defense

Jeff Serfass has successfully defended and made the required modifications to the text of the master's thesis for the M.S. during this Fall semester 2022.

Master's Committee
(Please sign and date beside your name)

Mentor:
Dr. M. Alper Sahiner ______________________________

Committee Member:
Dr. Weining Wang ______________________________

Committee Member:
Dr. Stephen Kelty ______________________________

The mentor and any other committee members who wish to review revisions will sign and date this document only when revisions have been completed. Please return this form to the Office of Graduate Studies, where I will be placed in the candidate's file and submit a copy with your final thesis to be bound as page number two.

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Table of Contents

Contents

List of Figures

Abstract

Fuel Cells using solid oxides for the electrolyte material, or Solid Oxide Fuel Cells (SOFCs), can operate at high temperatures and have many benefits when compared to other electrolyte material-based fuel cells. SOFCs can, however still have problems when operating at these high temperatures. (~1,000 degrees Celsius) At high temperatures, the SOFC electrolyte resistivity goes up making the ionic conductivity decrease and therefore a loss of performance. The inclusion of low level Yttria to Zirconium Oxide (the electrolyte material) has been known to help reduce the resistivity at high operating temperatures. In this study, a series of Yttria stabilized Zirconium Oxide thin films were grown by Pulsed Laser Deposition. The same series of films was deposited on Silicon, Zirconium and Alumina (Al2O3) substrates. Here, we will scrutinize these thin films using Secondary Ion Mass Spectroscopy or SIMS. SIMS is a depth profiling technique that is commonly used in materials characterization in the form of process monitoring, research and development or troubleshooting. We will be evaluating the compositions, film thicknesses, surface roughness, contamination and growth interfaces of these films, as well as correlating the SIMS data to the previous electrical measurements performed on these thin films.

Introduction

Fuel Cell Background

A Fuel cell is a system that produces electricity from a chemical reaction. A fuel cell consists of two electrodes, an electrolyte, and a catalyst. One electrode is positive, or the cathode and the other is negative, or the anode. The electrolyte carries charged particles from one electrode to the other. The catalyst is used to speed up the reaction at the electrodes.

Fuel cells are highly regarded for their low pollutant emissions. In the fuel cell, hydrogen is the fuel. Oxygen is also needed in the reaction. Due to this, the hydrogen and oxygen typically combine as the main byproduct in the form of water. In general, hydrogen atoms will enter the fuel cell through the anode and be stripped of an electron. This gives the hydrogen atoms a positive charge. The electrons that are stripped will provide the current through the wires of the device. The Oxygen, in some cases, enters through the cathode and combines with a stripped electron returning from the wire circuit and a positively charged hydrogen atom that has passed through the electrolyte. In other cases, the oxygen enters through the cathode and then travels through the electrolyte to the anode where it combines with a hydrogen ion. In either case, the hydrogen and oxygen combine to form water and are drained from the cell.

The electrolyte is critical, as it dictates which ions pass between the anode and cathode. The chemical reaction that produces electricity depends on the proper ions and will be disrupted if the electrolyte is not discriminating against unwanted ions. Because there is no combustion involved with the fuel in a fuel cell, there is not as much loss of energy to heat and there is not the same limitations as a combustion engine for instance. Additionally, any energy that is lost to heat in a fuel cell can also be harnessed to increase the devices efficiency.

Different Fuel Cell Types

One of the downsides to fuel cells is that they are expensive to make and can be very complex to design. Researchers are working on developing all different shapes and sizes of fuel cells to improve the cost, efficiency and reliability of fuel cells to make them more viable as an alternative energy source for the masses. The choice of electrolyte material is one of the main factors in a fuel cell's performance and design. Researchers developed fuel cells that use liquid electrolyte materials. These are alkali, molten carbon and phosphoric acid. Solid electrolytes have also been developed in the form of proton exchange membranes and solid oxides. These electrolyte materials will also dictate what type of fuel is needed. (i.e. purified hydrogen or hydrogen with impurities) The type of fuel will then dictate the temperatures needed to run efficiently. (i.e. molten carbon electrolyte fuel cells run hot) Liquid electrolyte materials may require pumps.

SOFC's and purpose of study

Solid Oxide Fuel Cells or SOFC are highly regarded due to some key features they offer. SOFCs are modular and scalable. They can also use a variety of fuel types and even tolerate low levels of impurities in the fuel. They are stable at high operating temperatures, but still reduce unwanted carbon and oxygen bonding that produces harmful CO2 gas. Because of their high operating temperatures, SOFCs can also produce hot water or steam that can then activate microturbines or gas turbines to produce electricity and further improve the efficiency of the system while also offering more applications of the device. Additionally, the production of the electrolyte for SOFCs can be more efficient and cost effective, as the epi growth market is very mature and well understood.

SOFC's typically use calcium or zirconium oxides as the electrolyte material. They require running temperatures of ~1,000 degrees Celsius. They output up to 100kW. There is no need to reform the hydrogen fuel at these temperatures. Solid electrolytes also cannot leak; however, they can crack. One solid oxide used is zirconium oxide. Efforts are being made by researchers to improve the lifetime and performance of these types of electrolyte materials. Zirconium oxide has volume changes and possible mechanical stress or failure due to phase transition during the heating and cooling process. By stabilizing the zirconium oxide with yttrium nano particles followed by diffusion of said particles or low-level yttrium during the growth of the oxide, one gains the ability to slow the degradation of the solid oxide electrolyte. YSZ (Yttria stabilized Zirconia) is the most common solid oxide material used as an electrolyte in SOFCs. YSZ demonstrates better ionic conductivity than other solid oxides at the operating temperatures of SOFCs. The increase in ionic conductivity correlates to an increase in yttria percentage to a point where the ionic conductivity saturates and then decreases. Optimal yttria is around 8 Mol percent. YSZ also offers good thermal and chemical stability, higher than that of other solid oxides used as electrolytes in a fuel cell.

Overview of study

In this paper, we evaluate YSZ grown by puled laser deposition or PLD. The YSZ was grown with different yttria percentages ranging from 1% to 10%. The YSZ was grown on three different substrates at all the different compositions. The main technique used was secondary ion mass spectrometry or SIMS. Additionally, X-ray photon spectroscopy or XPS was used as well as stylus profilometry. We evaluate the composition, contamination, growth interface and film thickness between the different films grown on the three different substrates. We also look at the film uniformity of the growth technique.

The YSZ growth goal was to incorporate specific amounts of yttrium in each film. The films targeted yttrium incorporation of 1%, 3%, 5%, 7%, 8% and 10%.   This series of six growth conditions was replicated on each of the three substrates. The substrates used were silicon (Si), alumina (Al2O3) and zirconium (Zr). All films were grown at the same temperature of 800C using pulsed laser deposition.

PLD

Pulsed laser deposition or PLD is a physical vapor deposition technique. A high energy laser is directed into a vacuum chamber toward a target material. The target material is composed of the material which is to be deposited on a given substrate. The targets can be a purchased material of desired composition or can be made using the proper ratios of raw materials and forming them into a “pellet” or “target”. The high energy laser hits said target and immediately vaporizes a small portion of the target. The target absorbs the energy from the laser and causes evaporation and plasma to form from the target and expand in a cloud-like region called the “plume”. The plume contains energetic atoms, ions, electrons and molecules that then get deposited on to the typically heated substrate. Orientation of the target and substrate is crucial for the deposition process. The substrate must be centered above the target such that the plume that is created will expand upward and uniformly deposit on the substrate. In most case the target is centered on a rotating stage for uniform coverage of the laser on the target. The term “pulsed” in PLD is used because the laser is not static. It is turning on and off many times per second. The laser turns on and hits the target, creating a plume and then turns off. This process happens repeatedly in a short amount of time and hence the “pulsing” of the laser. PLD can be done at high vacuum or ultra-high vacuum (UHV) pressures. UHV is preferred for lower atmospheric contamination incorporation in the films.

The PLD deposition tool used to grow the YZO films in this study was a TuiLaser made by PVD products. The laser is a 248-nanometer wavelength ultraviolet Krypton Fluoride Excimer Laser. The laser voltage was between 20-30kV. The laser operating frequency was 5Hz while the laser energy was 110mJ. The deposition chamber had a base pressure of 5e-6 Torr. The chamber was heated to 20 degrees Celsius. The target used was 6cm in diameter.

SIMS introduction

The main technique used to evaluate these films in this paper is secondary ion mass spectrometry or SIMS. SIMS is an analytical technique where a focused ion beam is accelerated at a thin film or sample of interest. The ion beam hits the surface of the sample and ejects material from the collision. (a process called “sputtering”) The ejected material is made of neutral atoms and molecules as well as charged atoms and molecules. The charged atoms or ions are considered “secondary ions” as they are created from the primary ion beam. The secondary ions are then electronically focused into a mass spectrometer that can then measure the mass of each ion. The primary ion beam will raster over a given area on the order of hundreds of square microns and continually eject secondary ions as the primary ion beam continues to sputter away material. What results is a depth profile of whatever masses are being monitored by the SIMS software. This makes SIMS a very useful technique as it can profile depth profiles of composition or bulk material of the sample or depth profiles of dopants and or contamination in the sample. SIMS can also be tailored to the need of the sample. Very thin samples can be analyzed with a low energy primary ion beam where thick samples can be evaluated with higher energy primary ion beams. SIMS is a destructive process, as it is removing material during the analysis. SIMS requires UHV conditions for optimal results.

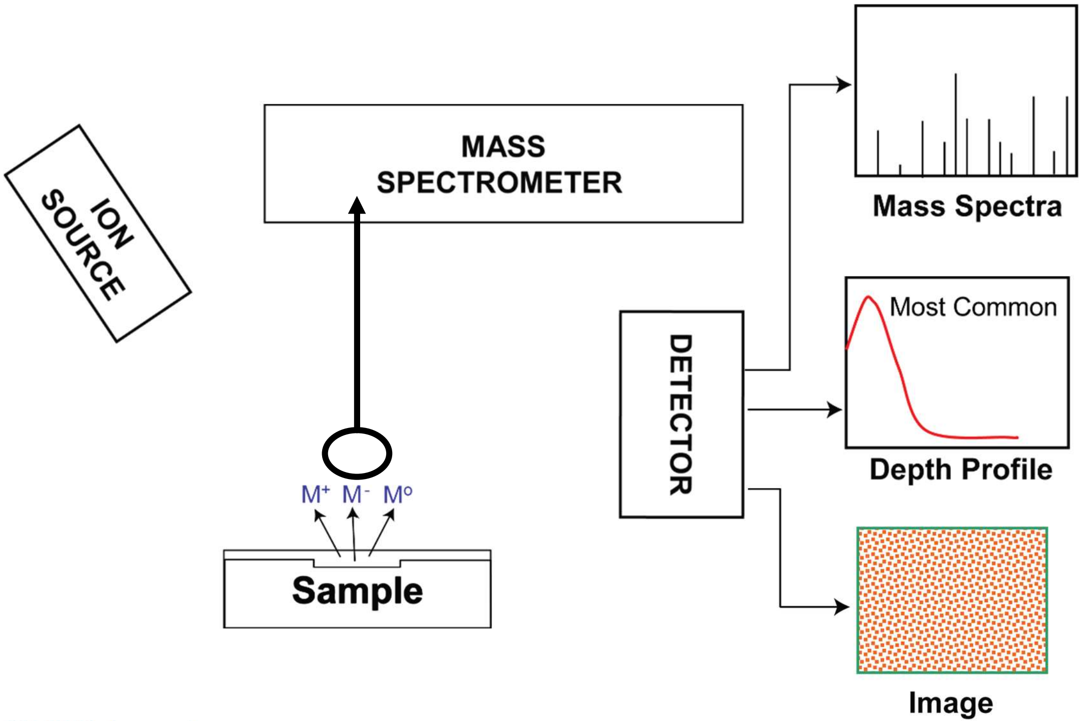


Figure 1: SIMS Schematic

(Schematic from citation #21, used with permission)

Types of SIMS

There are multiple different types of SIMS. SIMS as a technique originated from spark source analytical techniques as static SIMS. Static SIMS is where the primary ion beam is shot at a sample creating secondary ions. Then this set of secondary ions is analyzed by a mass spectrometer. This technique is used for only for the very surface of the a given sample. In dynamic SIMS, the primary beam is continuously sputtering material from the sample as the secondary ions are being analyzed, creating a depth profile of the material based on the elements being monitored.

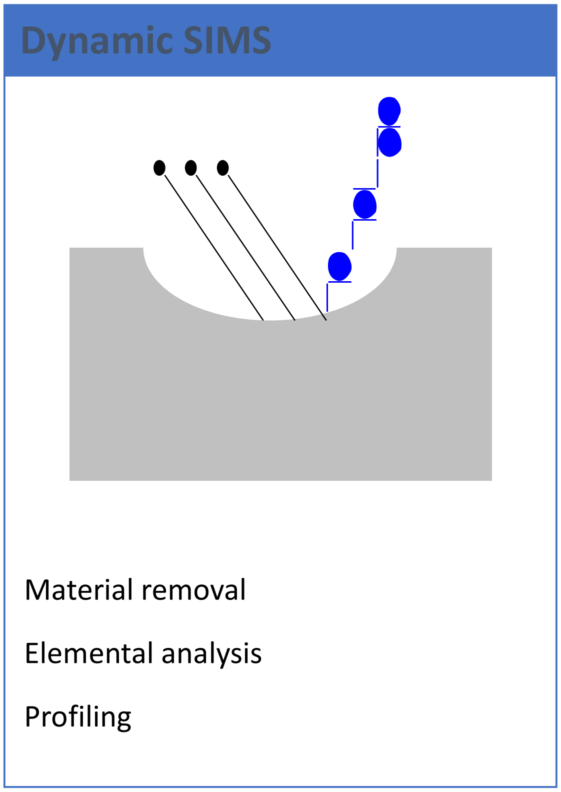


Figure 2: Schematic of Dynamic SIMS

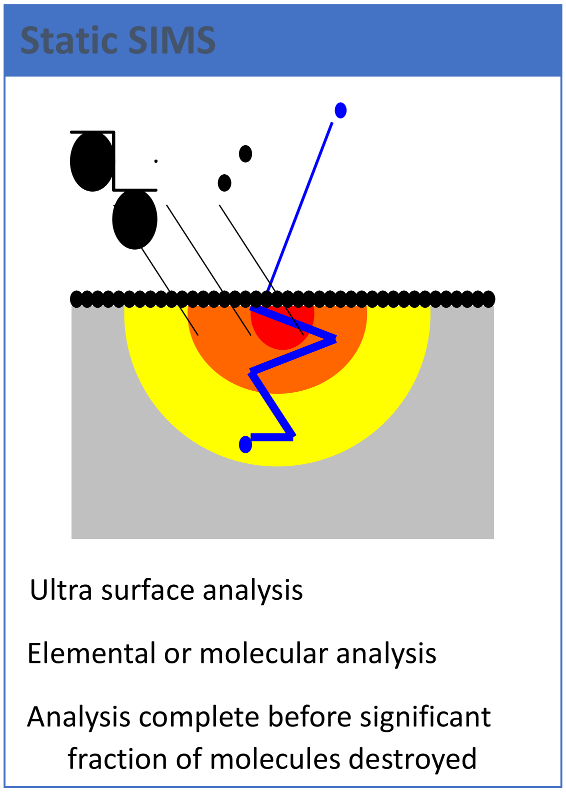


Figure 3: Schematic of Static SIMS

(Schematics from citation #19, used with permission)

There are three main types of dynamic SIMS. Magnetic sector SIMS, quadrupole SIMS, and Time of Flight (TOF) SIMS. Magnetic sector SIMS uses very strong magnets to discriminate secondary ions and measure only the ion of interest. Quadrupole SIMS sends the secondary ions into a small chamber with four charged rods where the ions bounce around between the four rods and then are discriminated against using the ion’s charge to mass ratio in order to measure the ion of interest. TOF SIMS is exactly what it sounds like, as it uses the actual time it takes for the secondary ion to travel from the sample to the analyzer. Based on the time it takes to travel, one can calculate the mass of the ion.

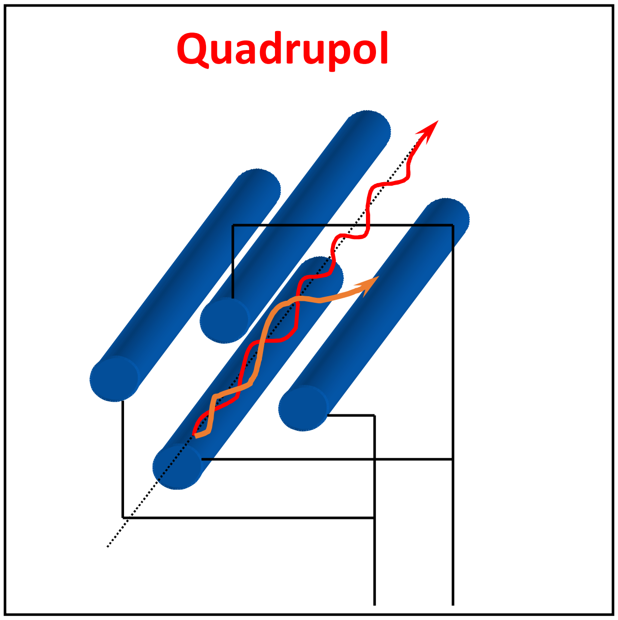


Figure 4: Image of Quadrupole Mass analyzer

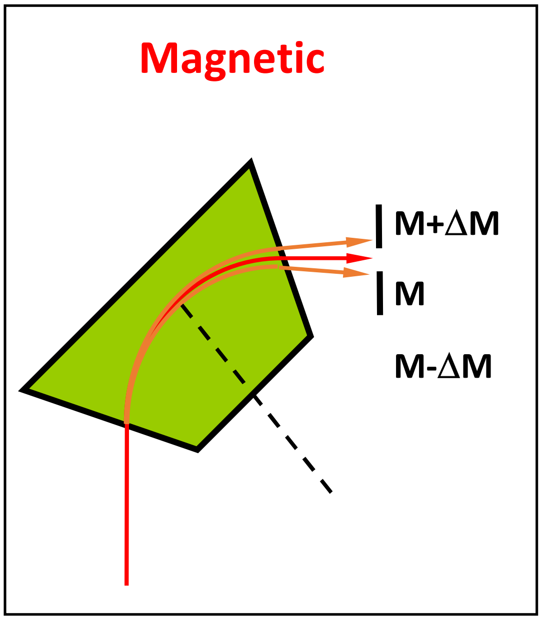


Figure 5: Image of Magnetic sector Mass analyzer

(Images from EAG Labs, 2010, used with permission)

TOF

Time of flight SIMS or TOF SIMS is considered static SIMS. This is because the primary ion beam is not continuously sputtering while the secondary ions are being measured. Instead, the primary ion beam is pulsed and then all secondary ions are analyzed. Then the process is repeated. Each pulse will produce many secondary ions and effectively a full mass spectrum, which will travel through an electronically predetermined path to the analyzer. The time it takes for the secondary ion to reach the detection will inform what mass the secondary ion or cluster is. (a cluster here is a molecular ion) Lighter masses will reach the detector first and heavier ones last. TOF SIMS is considered more of a “very near surface” technique and is not well suited for depth profiling. TOF SIMS is also particularly used for the analysis of organic materials, for which other types of dynamic SIMS are not efficient at analyzing.

Magnetic sector

Magnetic sector SIMS instruments are the most widely used. The primary ion source on these instruments is either a cesium ion gun or an oxygen ion gun. Both can produce either a positively or negatively charged ion beam. The primary ions hit the sample surface and start to produce secondary ions from the sample. These secondary ions are then electronically focused into, what is call the “magnetic sector”, which will bend the secondary ions around a curve. At the end of the “curve”, there is a small slit where the secondary ions can then pass through. Depending on the mass of the secondary ion, some ions will curve too much and hit the wall, while others won’t curve enough and still hit the wall of the magnetic sector. Only the mass of the ion of interest will be able to pass through the slit and proceed on to the detector. The magnetic sector will be tuned according to what ions are of interest. These instruments have very high mass resolution, meaning they can easily distinguish between one mass and another. In SIMS, there can be molecular mass interferences depending on the material one is analyzing. Additionally, there a false reading from an element with high intensity to another element that is 1 amu away in mass. Magnetic sector SIMS does not run into these issues because of the high mass resolution of the system. Magnetic sector SIMS also has high transmission, meaning it is more sensitive and can therefore see lower levels of a given ion. This translates to the detection limits being better in Magnetic sector SIMS. The detection limit is literally the lower limit at which you can detect the ions.

Magnetic sector SIMS does have some drawbacks as well. The peak switching of the magnetic sector is slow. Switching which mass you are looking at is not very quick with a Magnetic sector SIMS instrument. Because of this, fewer elements can be monitored in each profile. Traditionally this was not an issue, as SIMS was made popular by analyzing single element implant profiles for p and n doped Si for transistors. Now with complex III/V materials with many dopants, the ability to monitor elements for composition, dopants and impurities simultaneously is priceless. Magnetic sector SIMS cannot do this efficiently. Another downside to magnetic sector SIMS is the energy limitations of the primary ion beam. Low beam energies are more difficult to use on magnetic sector SIMS instruments. This results in poorer depth resolution, as high primary beam energies will distort the depth profile through "knock-in" effects. Knock-in effects are from the high energy beam knocking elements deeper into the material while also ejecting secondary ions. In the depth profile, this will translate to more broadened interfaces and artificial "tails" of say and implant profile for example. When dealing with insulating samples, magnetic sector SIMS instruments can have trouble "charge compensating" for the insulating material. When a sample is insulating, it is hard to get any signal from a given secondary ion. Luckily, due to the high energy and therefore high sputter rate along with the high transmission of the magnetic sector SIMS instruments, they are generally not as affected by insulating layers in a material and really only have trouble with a sample that is itself very insulating.

Quadrupole

Quadrupole SIMS was the latest type of SIMS to be developed. It uses the same principle as magnetic sector SIMS. The primary ion source is typically cesium or oxygen tuned to either positive or negative ions. The primary ion source is usually set at a 60-degree angle of incidence. The primary ion beam is focused through electronic lenses and onto the sample where it begins sputtering material and creating secondary ions. These secondary ions are then similarly electronically focused into the actual quadrupole. Inside the quadrupole there are four "rods" where the secondary ions bounce around between the diagonally oppositely charged rods.

Based on the mass to charge ratios of the secondary ions, the rods are charged accordingly to only allow the element of interest past. The one benefit of this type of SIMS is the fast peak switching speed. Meaning the quadrupole can switch between what element it is looking at very fast. This allows for many elements to be monitored simultaneously in one profile. Another benefit of quadrupole SIMS is its ability to charge compensate for insulating samples. There are built in electron guns that can be imaged and then focused on the sample to provide ample conductivity (in the form of raw electrons) for the transmission of the secondary ion signal. These electron guns can also be tuned according to the insulating material one is analyzing. One of the largest benefits of quadrupole SIMS is that their primary ion guns are good for low energy primary ion beams. Magnetic sector SIMS usually uses 5 – 10keV for their primary ion energy, while quadrupole SIMS can operate between 500eV – 5keV. This allows for less energetic distortion of the depth profile. (less “knock-in”) This also makes for easier shallow depth profiles.

The downsides of quadrupole SIMS are its mass resolution and its lower transmission. Although the mass resolution is pretty good on quadrupole SIMS instruments, there is a susceptibility to molecular mass interferences. Since quadrupole SIMS can easily monitor multiple masses at once, one tends to monitor multiple isotopes of a given element in order to confirm there were no mass interferences. The transmission is also lower than that of magnetic sector SIMS. This translates to poorer detection limits. There are trades offs when choosing what SIMS instrument is best for a given analysis.

Cameca IMS-6f

Figure 6: Image of Cameca 6f SIMS instrument (magnetic sector)

PHI Adept 1010

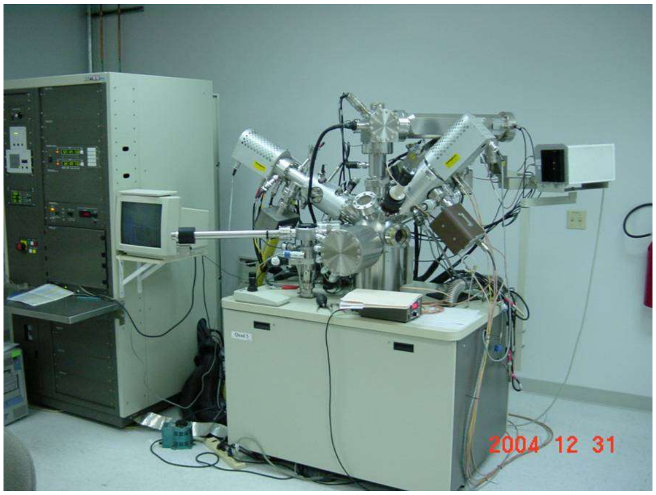


Figure 7: Image of PHI Adept 1010 SIMS instrument (quadrupole)

(Images from EAG Labs, 2010, used with permission)

SIMS as an analytical technique

SIMS is a great analytical tool for research and development, process monitoring and troubleshooting. SIMS is widely used as an analytical technique by Epitaxy growers and vendors alike. With SIMS, the main benefit is the amount of information you can get in one single technique. That is not to say it is the best technique for any specific goal, but possibly one of the better techniques for an overall analysis of thin films. Using SIMS as an analytical technique can provide a wide variety of information. Initially SIMS was utilized for the purpose of evaluating ion implantation into silicon for early transistors. Developments in the SIMS instrumentation, SIMS data analysis, and new demands from the market have furthered the capabilities of SIMS to more than depth profiles of ion implants into silicon. SIMS is now used for everything from quantified compositional depth profiles of complex semiconductor thin film layers structures to low level impurity analysis. Accurate dopant concentrations can be measured while simultaneously measuring low level impurities and layer compositions to offer more information than standard surface analysis techniques. SIMS offers better depth resolution than many techniques with detection limits as low as 1e12-1e14 atoms per cubic centimeter. This makes it ideal for thick complex epitaxial layer structures like vertical cavity surface emitting lasers or triple junction solar cells. With improved data processing calculations, SIMS can also provide accurate layer thicknesses.   SIMS measures total amount of an element, so the results will differ from certain other techniques; like ones that measure electrically active dopants for example.

There are two main modes of analysis in quadrupole SIMS. Positive or negative are the two options for the secondary ion analyzer. The mode at which one performs the analysis depends on the element in question. Some elements yield more negative ions during the sputter process while others yield more positive ions. In some rare cases, elements give a very low conversion rate into either type of ion. While there are many reasons to set up the quadrupole to look at either type of ion, it really depends on the element you are looking at and the material that element is in. Although not universally true, composition measurements are typically done monitoring positive ions while dopant and contamination analysis are usually done monitoring negative ions.

There are some downsides to using SIMS as an analytical technique. SIMS does not provide any electrical information on the samples being analyzed.   Complete devices can then not be evaluated for performance beyond theoretical values. SIMS is a destructive technique in that it destroys the area of the sample that is being analyzed. One must sacrifice the sample if SIMS is a desired technique. SIMS is not a standardless analytical tool, meaning for proper quantification, there needs to be a reference material. SIMS cannot measure elements without referencing a sample with known amounts of said element. This becomes a problem for the evaluation of complex III-V semiconductor materials due to the many layers of different composition with many dopants and many unwanted impurities. The need for proper reference materials in SIMS and the complex nature of how different elements react to the SIMS sputter process based on the material they are in make the SIMS data processing very complex and a large hurdle in order to make SIMS useful.

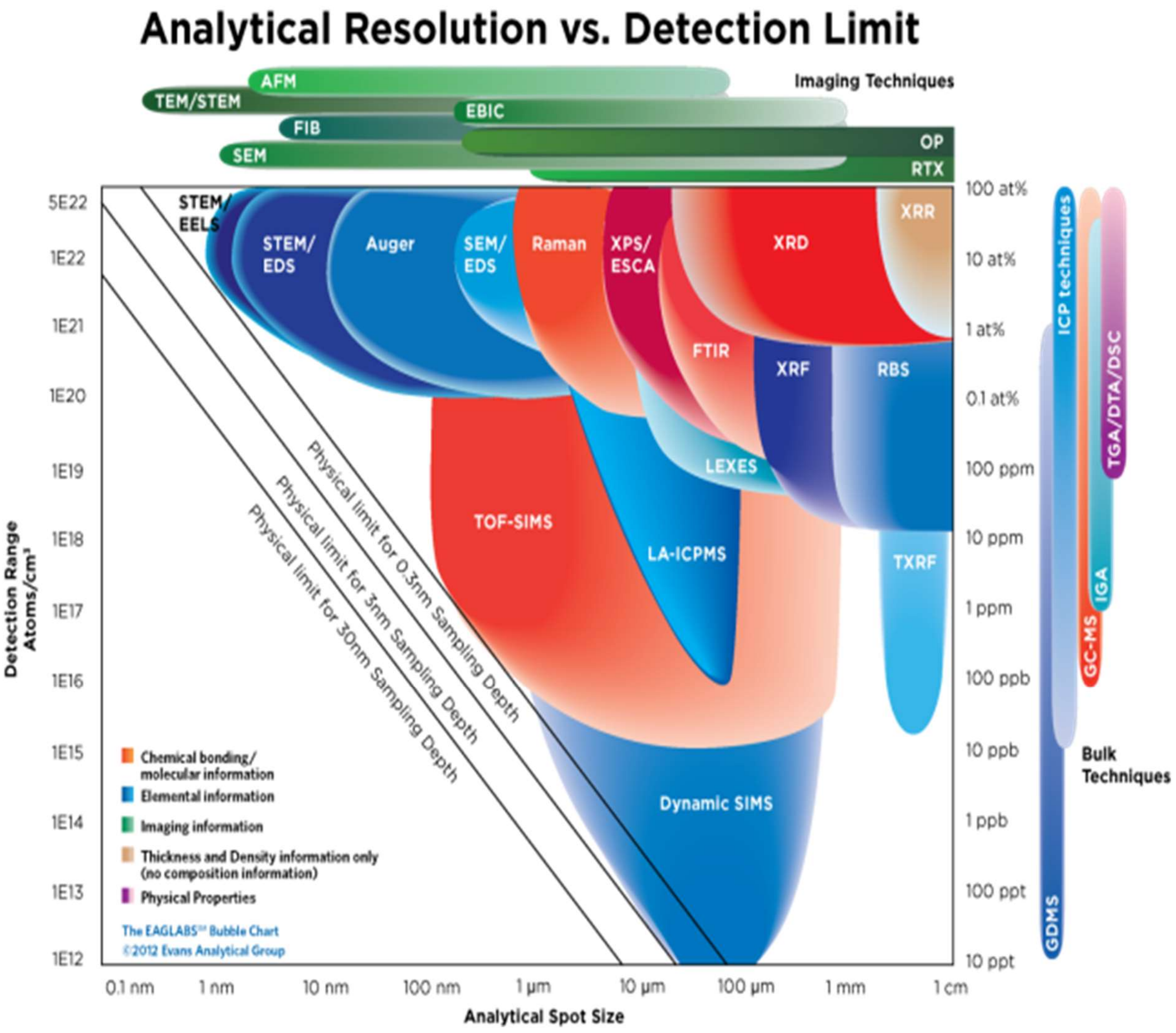


Figure 8: Graph depicting analytical resolution vs detection limit and analytical spot size of material characterization techniques. (Image from EAG Labs, 2016, used with permission)

PHI Adept 1010 Instrument

In this research, a quadrupole SIMS instrument was used. The first quadrupole SIMS instruments were developed in the 1970s. Early SIMS instruments that did not use quadrupole analyzers were developed in the 50s in Vienna and at RCA Laboratories in Princeton New Jersey. In the early 60s, two more SIMS instruments were developed. One instrument was developed in the US for analyzing moon rocks and the other was developed in Orsay for a PhD thesis project. All these early instruments used magnetic sector style of a mass analyzer and Argon as the primary Ion beam. In the 1970s Charles Magee and colleagues (from RCA labs) developed a SIMS instrument that used a quadrupole mass analyzer. These beginnings of SIMS as a technique saw the instrumentation as one-off designs and experimental features. In 1969, a company called Physical Electronics or PHI was established as an off shoot of the university of Minnesota. Originally an analytical laboratory for Auger electron spectroscopy, PHI continued to develop instrumentation and became a vendor for analytical instruments such as XPS, dynamic SIMS, and TOF SIMS in addition to Auger electron spectroscopy. PHI introduced its first commercial quadrupole SIMS instrument in the form of their model 6300 Quad SIMS instrument. As they continued to improve on the design of their analytical tools, they released the model 6600 Quad SIMS instrument. In the early 90s, PHI introduced their PHI ADEPT 1010 Quad SIMS instrument. This is their most advanced SIMS instrument to date. The Instrument used for the experiments in this paper was a PHI ADEPT 1010 SIMS instrument.

The ADEPT 1010 SIMS instrument functions on the same principles of the earliest PHI Model 6300, however the electronics that control the instrument are much improved. Additionally, there are new features that allow for more flexibility and possibility in what types of analysis can be done as well as the ease of executing the analysis. The 1010 instrument has electronically controlled secondary ion optics. The secondary ions can be manipulated more than in any previous model of Quad SIMS instrument. One of the largest improvements to the instrumentation is the motorized stage. The stage, where the mounted sample(s) is placed, can be programmed to drive to specific location on a given sample. This allows for programmable/automated analysis. The improvement of efficiency is critical for materials characterization laboratories and even internal process monitoring laboratories. The 1010 SIMS instrument also allows for adjusted quadrupole analyzer conditions (secondary ion optics) for each element in a profile. This allows for fine tuning of an analysis and individual optimization of each element. The primary ion beam of the 1010 instrument remains largely unchanged from the earliest SIMS instruments with only the addition of some electronic focusing lenses as well as an electronic extraction field for drawing more current from the primary ion beam source. These improves features on the PHI ADEPT 1010 SIMS instrument have made it the industry leader and top choice when it comes to analytical needs related to quadrupole SIMS.

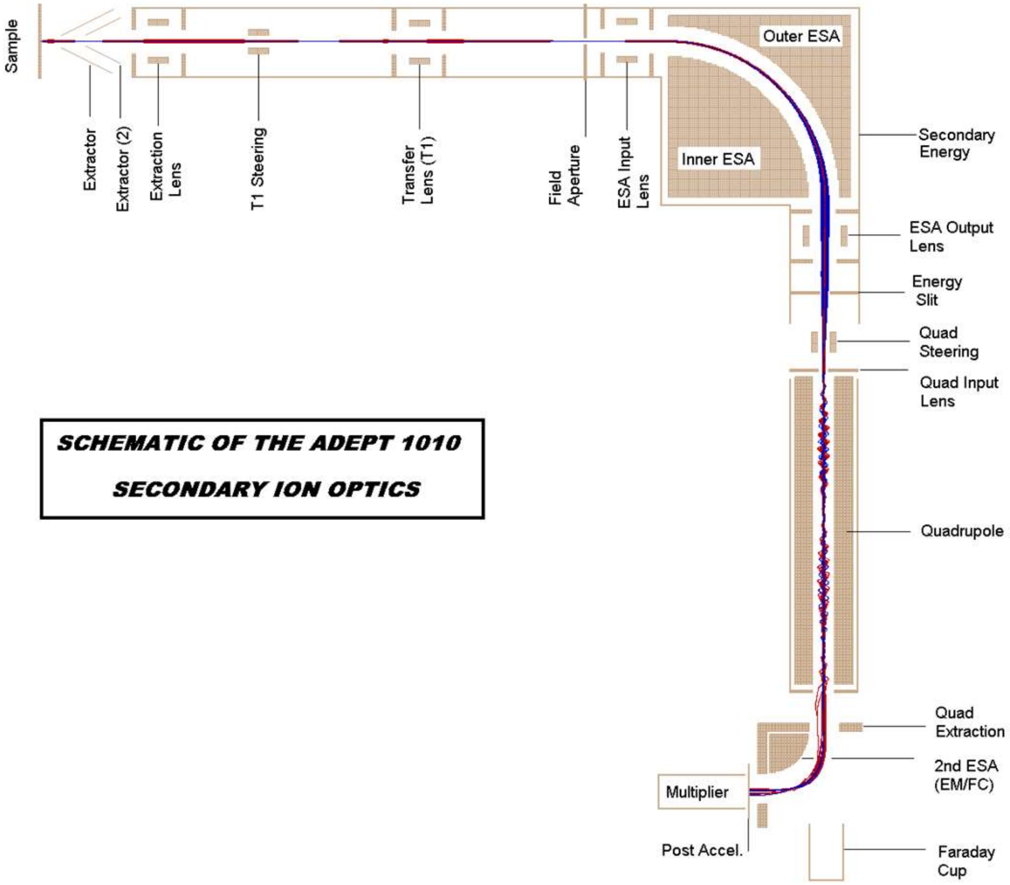


Figure 9: Schematic of the PHI Adept 1010 secondary ion optics

(Images from EAG Labs, 2015, used with permission)

SIMS sample mounting

When mounting a sample for SIMS, the sample is generally cleaved to a manageable size and then cleaned to be mounted on a sample holder or puck. The sample size can vary depending on the size of the holder or what other samples need to be mounted along with it. The minimum size for a sample in quadrupole SIMS is on the order of 1 square millimeter. A sample smaller than that is usually separately mounted on a piece of conductive material such as silicon or gallium arsenide so it can be handled easier and then mounted onto the puck. The samples are cleaned with methanol and then pasted to the sample puck. The pasted used can vary, but needs to be electrically conductive, so a silver or nickel pastes is typically used. After pasting the cleaned sample onto the holder, the sample is placed into an oven at 150 degrees Celsius for an hour at minimum. This is to evaporate any moisture in the paste. Vacuum ovens can be used to reduce this time to about 20 minutes. The sample holder can then be loaded into the introduction chamber of the SIMS instrument where it will receive a half hour pump down at the 1e-6 Torr pressure range. The sample holder or puck is stainless steel. The sample holders also need to be cleaned before and after the SIMS analysis. This cleaning process is usually just placing the puck into a methanol bath and sonicating for 20 minutes. On the ADEPT 1010 SIMS instruments, a 2-inch diameter, circle sample mounting puck is used. In analytical laboratories, up to 30 samples are mounted on a puck at a time for analysis. The puck itself has a faraday cup in the center for measuring the primary beam. This is used not only to check the beam current, but also to tune the primary ion beam to the specification needed for a particular analysis.

Beam tuning

Tuning the primary ion beam is necessary for all analysis. The quality of the primary ion beam will reflect the quality of the data produced by the analysis. Some analyses do not require a finely tuned beam (bulk dopant analysis for example), but most semiconductor work requires a primary beam with sharp focus and good current density. If a primary ion beam is too large with respect to the sputtered area size, the beam will overlap on its rater paths and sputter the center of the sputtered area faster than the sides of the SIMS crater. This will yield thick sloping side walls of the SIMS crater. When this happens, the secondary ion analyzer can begin to pick up signal from the crater side walls and will give a SIMS artifact known as “crater edge” artifacts.

This can be mitigated by electronically limiting the area from which the SIMS analyzer is taking data (electronic gating), but if the beam is large enough with respect to a given SIMS crater size (raster size), no amount of electronic gating will suffice. So, if the beam is too large or the crater size too small, these artifacts will appear in the SIMS data. A typical gated area of a SIMS analysis is the central 5-20% of the overall sputtered area.

When tuning a primary ion beam, one must select the beam energy desired (typically 1-5keV) and then tune the beam to a chosen current. Once the desired beam energy and current are set, then one can begin focusing the beam. There are multiple ways to fucus a primary ion beam. One method is simply imaging the faraday cup (raster the beam over the faraday cup) using the beam and then adjusting the focus to get a sharp image. More fine tuning can be done using a sample such as SiO2/Si. In this type of sample, the top layer of SiO2 is generally colored. When the beam sputters through to the Si below, you can see an image of the beam. This is not done in a rastering mode, but rather using a point probe of the primary ion beam. This will show what the actual beam looks like. From there, fine focusing optics can be adjusted to achieve an optimized focusing of the primary ion beam. One issue with tuning a finely focused primary ion beam is that the impact of the fine adjustments on the cesium beam are not always optically obvious. For example, once the beam is mostly focused, the fine adjustments don't make a huge difference and make it difficult to tell what settings will translate into the best beam for data acquisition. Sometimes, when a focused beam is a little larger than desired, one may be inclined to focus the beam further. At first appearance, the further focused beam appears tighter and smaller (more focused), however in data acquisition, one may notice the beam is overly focused and therefore getting low intensity "flares" off the main beam. This happens because the focusing lenes are trying to focus a beam beyond its maximum focus and begin to "squeeze" the beam such that it crosses over on itself. Sometimes this can be seen when imaging the beam for tuning as mentioned above, however if the "flares" on the beam are of low enough intensity, the are not optically seen when imaging. One way to check to make sure your focused beam is not overly focused is to shoot a point probe (no raster of the beam) at a sample while looking at an element that is typically found on the surface of most samples in a high amount. Oxygen is a good element for this purpose. When you shood a point probe at a sample looking at Ox, one will typically see a high intensity of Ox signal from the quadrupole and then see it begin to drop quickly after the beam sputters through the sample's native oxide. The potential "flares" in the primary beam will sputter this native oxide as well and yield more intensity in the Ox signal. Do help reduce or remove these "flares", one can adjust the focusing settings while sputtering with a point probe and looking at the Ox signal. As the fine focusing settings are adjusted, the user is looking for a lower intensity of the Ox signal. Once the minimum Ox signal is reached, one can be confident the beam focusing is optimized for sharpness.

Another aspect of "beam tuning" is beam uniformity. The primary ion beam must be uniform in intensity to insure the uniform sputtering of epi layers. If a multilayered sample is being sputtered with a nonuniform beam, one will begin seeing intensity of a layer below the current layer being sputtered. This will translate into the layers being "blurred/smeared/broadened" in the data. Achieving good resolution with sputter depth (depth resolution) is one of the main benefits of SIMS when compared to other analytical techniques. Beam uniformity is also affected by the focusing as well as the condition of the primary ion source itself. If the primary ion source settings are not optimized, one will get nonuniform emission of cesium ions from the frit of the cesium source. This will translate to "hot spots" or areas in the beam that are of higher intensity and therefore nonuniform sputtering of a given sample.   Once the primary ion source is optimized for uniform emission of ions, one still must ensure the tuned beam is uniformly sputtering the sample surface. A finely focused beam may have a slight intensity gradient. Any intensity gradient in the primary beam must be adjusted to be concentric, which is not trivial, since the primary ion source is hitting the sample at an angle of 60-degrees.   A uniform beam will yield good depth resolution of a multi layered structure. This is very important in samples such as GaAs/AlGaAs VCSELs. (Vertical cavity surface emitting lasers) When the primary beam is uniform in intensity, the bottom of the SIMS crater that is left after the analysis should be very “flat”. This is commonly known as “crater bottom flatness”.   The quality of the data acquired in SIMS is directly related to the quality of the primary beam tuning and the crater bottom flatness.

SIMS quantification

Reference materials

SIMS is not a standardless technique, meaning SIMS cannot quantify an element from scratch. SIMS needs a reference material that has an element of a known amount in order to properly quantify said element. Typically, these reference materials are ion implant samples. Ion implantation is a very mature process and generally trusted for its accuracy. With a reference material that has arsenic implanted into silicon, SIMS can then quantify arsenic in silicon, based on the known amount in the reference material. For composition quantification, reference films are usually grown with a desired composition using MBE (molecular beam epitaxy) or MOCVD (metal organic chemical vapor deposition) growth methods. This does, however mean that data acquisition is not limited to the samples of interest, but also includes any necessary reference materials.

In some cases, a multilayered reference material will be grown with various compositions and doping elements. Then this multilayered reference material will be quantified using individual reference materials for each layer composition and each doping element. Then the SIMS scientist can use this one reference material to quantify many different samples, leading to less time spent on the data acquisition of reference materials and more efficiency on the overall analysis/experiment.

Quantifying reference materials

Although ion implantation is relatively accurate, SIMS reference materials still need to be quantified for confirmation of the value of the element of interest. (i.e. implant does or doping level) SIMS can also utilize other standardless techniques to based quantification on. RBS or Rutherford backscattering is one technique frequently used to quantify SIMS reference materials. XPS or x-ray photon spectroscopy is another technique used to aid in the quantification of SIMS reference materials. SIMS overall accuracy is only as good as the accuracy of the reference materials used. When possible, utilization of NIST (national institute of standards and technology) certified reference materials is always preferred for SIMS.

RSF

The SIMS reference material will be analyzed and give the analyst a relative sensitivity factor or RSF for a particular element. This RSF will then be used to quantify the same element in the same material of a new sample with unknown amounts of said element. The raw intensity (counts per second) of the element is multiplied by the RSF and divided by the raw intensity of the matrix element. The matrix element is usually the bulk material that the element of interest is in. (i.e. Si would be the matrix element for As in an As implant into Si). This simple calculation will give the value of the element of interest in atoms per cubic centimeter concentration. SIMS will quantify the total value of an element and not the electrically active portion of a dopant or implant.

SIMS artifacts

SIMS quantification can be less trivial than simply running a reference material. The difficulty arises when the raw SIMS data suggests a feature or quality in the sample that is not real. These are generally referred to as "artifacts". These can be hard to identify if the false reading is not a known problem. SIMS artifacts are one of the most difficult aspects of performing and accurate SIMS analysis. One simple example of a SIMS artifact is seen in ion implants into silicon. At the surface of every epi film is a native oxide. Secondary ion intensity of a particular element changes depending on the composition of the layer it is in. For some ion implants, the implanted element is more sensitive and has a higher ion yield/intensity in the native oxide region at the very surface of the sample than it does in the silicon itself. This is because SIMS causes ion mixing and "knock in" some of the native oxide into the surface of the silicon making the very near surface behave more like silicon dioxide. Some commonly implanted elements have better secondary ion yield in SiO2 than in Si itself. This improved ion yield makes the raw data look like it has a higher amount of the implanted material near the surface of the sample before the typical gaussian implant profile is seen. This is not real and a SIMS artifact. An old technique to correct for this native oxide issue was to flood the sample with oxygen during the analysis so that the Ox rich region then continued through the entire analysis resulting in the sample ion yield of the implanted element throughout the whole SIMS profile. The same applies to the quantification of an element in a multilayered sample. Each layer will give a different ion yield for the same element. Utilizing multiple or multilayered reference materials can help account for this sensitivity change, however in a sample that has graded layers or layers where the composition is slowly changing, correction factors to the RSF of a given element is needed. In this way, SIMS has evolved to where the sensitivity changes are being corrected for at every data point for each element. This is all done in the SIMS data processing software.

Other common artifacts are mass interferences. This happens when the mass analyzer is looking at a combination of elements and there is a different combination of elements that add up to that same mass. For example, when looking at tellurium in a silicon doped indium-gallium phosphide sample, tellurium masses 128, 129 and 130 will have interferences from 69Ga + 31P + 28, 29 or 30Si. This happens often in complex III/V materials. The reason for monitoring a combination of elements is to increase the sensitivity and improve the detection limit of a particular element. Many times, atomic elements have poor sensitivity and are more effected by ambient backgrounds in SIMS vacuum chamber, but by monitoring them in combination with an element in high abundance, the sensitivity can increase. To compensate for these artifacts, a SIMS analyst will monitor additional isotopes of a given element or even monitor atomic elements to confirm general shape of a given profile.

False readings can be artifacts from the way a specific sample sputters or from defects in the sample. For example, SIMS roughens all samples to some degree as the sputtering process takes place, so if a sample surface is rough to begin with, individual layer interfaces will be seen as artificially broad in the SIMS data. This is because when the sputtering of a rough sample approaches a layer interface, the SIMS analyzer is seeing signal from the layer above and the layer below causing an early signal from the layer below and a lingering signal from the layer above. In SIMS, roughness translates into sputtering different heights of the sample at the same time and gets worse with sputter depth. Another similar but different artifact will be from defects in the growth of the sample. The defects in the crystallinity of the sample appear in various forms, but one form seen in gallium nitride materials is call a “V defect”. These are triangle or “V” shaped defects that originate from the epi growth on the substrate and are likely caused by lattice mismatching. These defects will not be seen everywhere on the sample, however if one does a SIMS analysis on the location of a V-defect, one will see a lingering signal of the layer or dopant from the above, already sputtered off, layer or dopant.

Other artifacts in SIMS data can be directly correlated to the primary ion beam energy. Roughening of a sample, as mentioned prior, will happen at all beam energies, but will be worse at higher energies. The more energetic the incident ion is, the more destruction it will doe and therefore the more distortion one will see in the SIMS data. Layer interfaces can be one area where primary beam energy artifacts can be seen most easily. The primary ion beam will “knock in” some elements at the same time it is ejecting secondary ions. This results in a more gradual slope of interfaces, different from the broadening artifacts discussed above. Here, the interface is still sharp and well defined, however as the intensity of an element drops, some of the element is still being “knocked in” to the sample deeper. The result is a more gradual slope of the falling element from the layer above already sputtered away.

Another deceiving aspect of SIMS data, however not an artifact per say, is the depth calibration of a sample. Particularly for multilayered samples, depth calibration is not trivial. Layers of different compositions sputter at different rates. One could use reference materials to set a sputter rate of a particular layer, however that would be inefficient. One option in a single layer sample, (i.e. SiO2/Si) would be to stop the SIMS profile at the layer interface and then measure the depth of that SIMs crater using stylus profilometry. This works quite well but is not realistic for a sample of many layers of various compositions. The solution here is to develop mathematical corrections to the sputter rate based on composition changes. For example, if a sample is a multilayer stack of GaAs/AlGaAs, one can use the sputter rate for GaAs and then based on the amount of Al in the AlGaAs layers, correct the sputter rate accordingly. This is identical to the RSF corrections to elements at each data point. Using this way of correcting for sputter rate changes, one can accurately quantify multilayer stacks of many different compositions as wells graded layers. These sputter rate corrections allow SIMS to agree well with techniques like TEM for layer thicknesses.

SIMS quantification using XPS

For the experiment discussed in this paper, there were no reference material available. Sample 20 (10% Yttrium) from the YZO/Zr batch of samples and sample 19 (10% Yttrium) from the YZO/Al2O3 batch of samples had XPS done on it to quantify the yttrium, zirconium, and oxygen. The XPS data was taken on a PHI XPS 5600 model instrument. The first attempt was not successful, as there was too much surface oxide on the sample. After sputtering ~6nm with an argon ion gun in the XPS instrument, the results were useful for quantifying the SIMS data. The data for sample 20 (10% Yttrium YZO on Zr) was forced to the values given in the XPS data and then those RSFs were used to quantify the YZO/Si batch of the samples. The one sample from the YZO on alumina substrates that was also analyzed with XPS for quantification gave more confidence in the precision of the quantification technique. Here the results between the two samples analyzed by XPS yielded relative sensitivity factors that were the same to within the SIMS error bar. (~ +/- 5 relative percent) This is not a huge surprise since XPS is a well-established technique for materials characterization. The concentrations in the substrates are not accurate. Sputter rate of the YZO films was set by stopping a SIMS profile at the YZO/substrate interface and then measuring that SIMS crater an applying that sputter rate to all the samples.

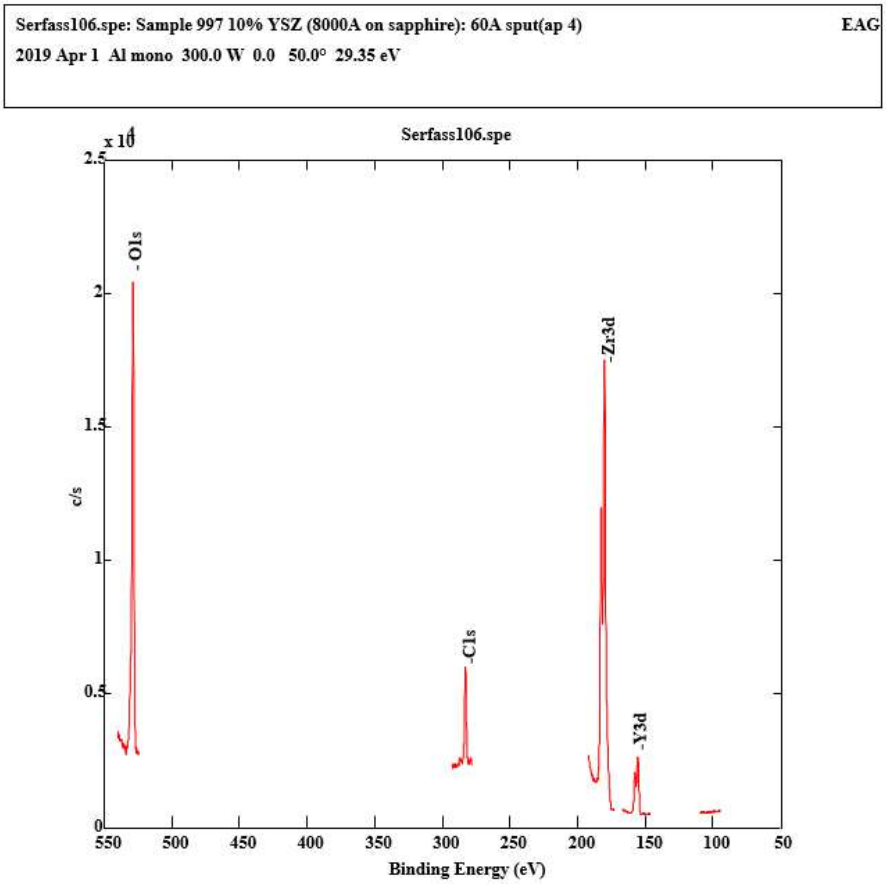


Figure 10: Full energy spectrum XPS data for sample 19 (10% Yttrium YZO on Al2O3)

(XPS data for this paper were acquired by Mark Denker, EAG Labs, 2019)

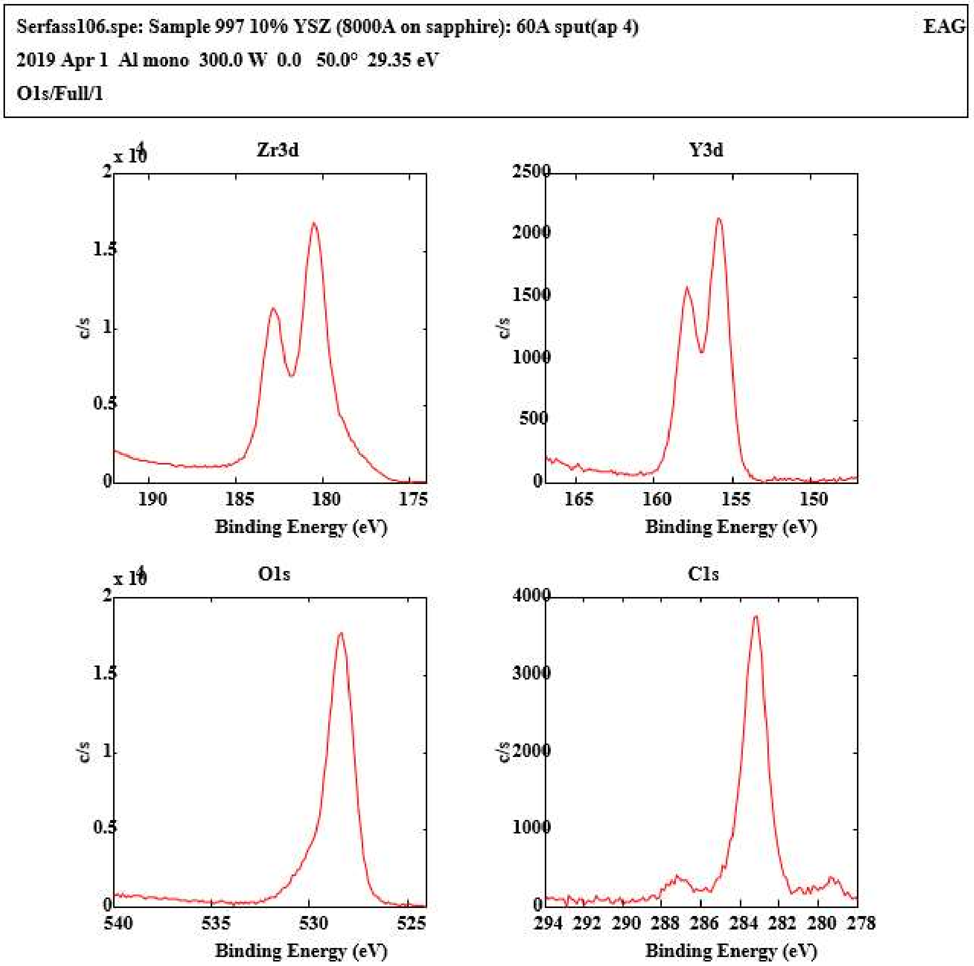


Figure 11: Zoomed in energy peaks XPS data for sample 19 (10% Yttrium YZO on Al2O3)

(XPS data for this paper were acquired by Mark Denker, EAG Labs, 2019)

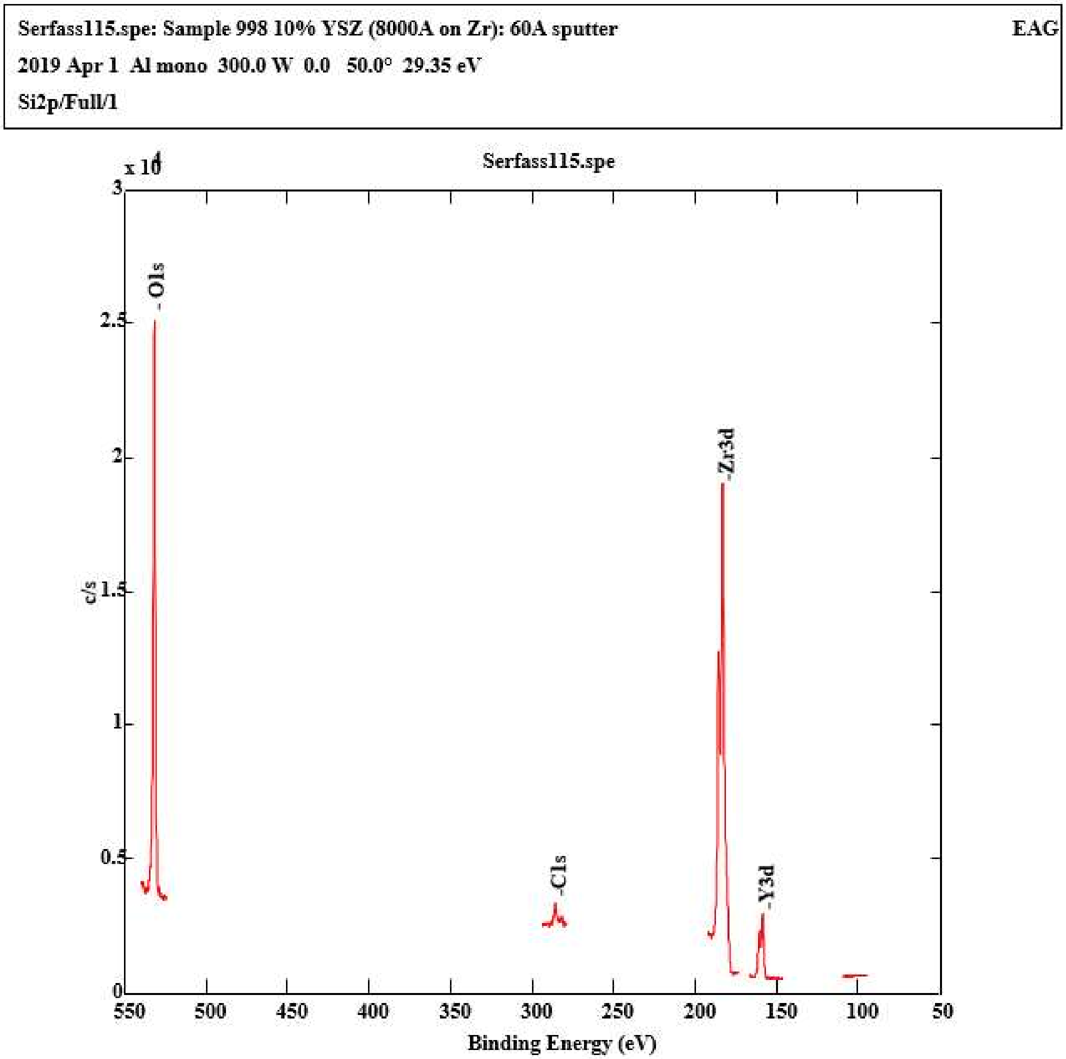

Serfass115.spe: Sample 998 10% YSZ (8000A on Zr): 60A sputter EAG
2019 Apr 1 Al mono 300.0 W 0.0 50.0° 29.35 eV
Si2p/Full/1

Figure 12: Full energy spectrum XPS data for sample 20 (10% Yttrium YZO on Zr)

(XPS data for this paper were acquired by Mark Denker, EAG Labs, 2019)

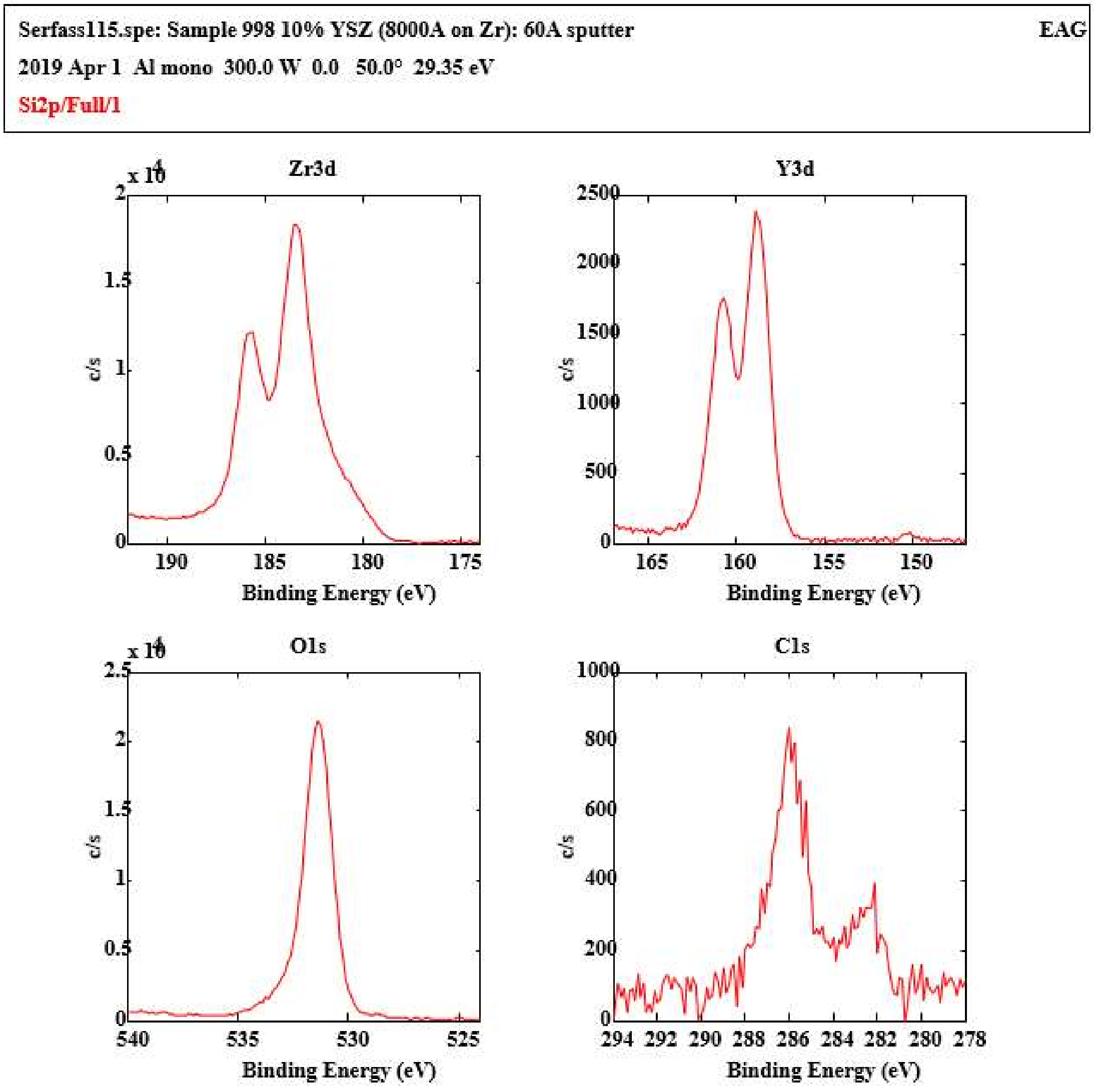
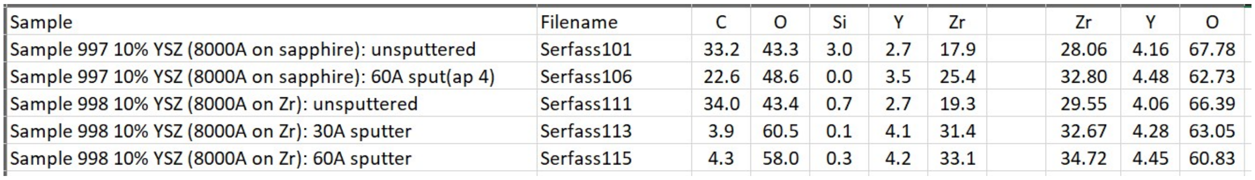


Figure 13: Zoomed in energy peaks XPS data for sample 20 (10% Yttrium YZO on Zr)

(XPS data for this paper were acquired by Mark Denker, EAG Labs, 2019)



Sample	Filename	C	O	Si	Y	Zr		Zr	Y	O
Sample 997 10% YSZ (8000A on sapphire): unsputtered	Serfass101	33.2	43.3	3.0	2.7	17.9		28.06	4.16	67.78
Sample 997 10% YSZ (8000A on sapphire): 60A sput(ap 4)	Serfass106	22.6	48.6	0.0	3.5	25.4		32.80	4.48	62.73
Sample 998 10% YSZ (8000A on Zr): unsputtered	Serfass111	34.0	43.4	0.7	2.7	19.3		29.55	4.06	66.39
Sample 998 10% YSZ (8000A on Zr): 30A sputter	Serfass113	3.9	60.5	0.1	4.1	31.4		32.67	4.28	63.05
Sample 998 10% YSZ (8000A on Zr): 60A sputter	Serfass115	4.3	58.0	0.3	4.2	33.1		34.72	4.45	60.83

Figure 14: XPS values for sample 19 and 20 used to quantify SIMS data. (60A sputter values used and C and Si excluded)

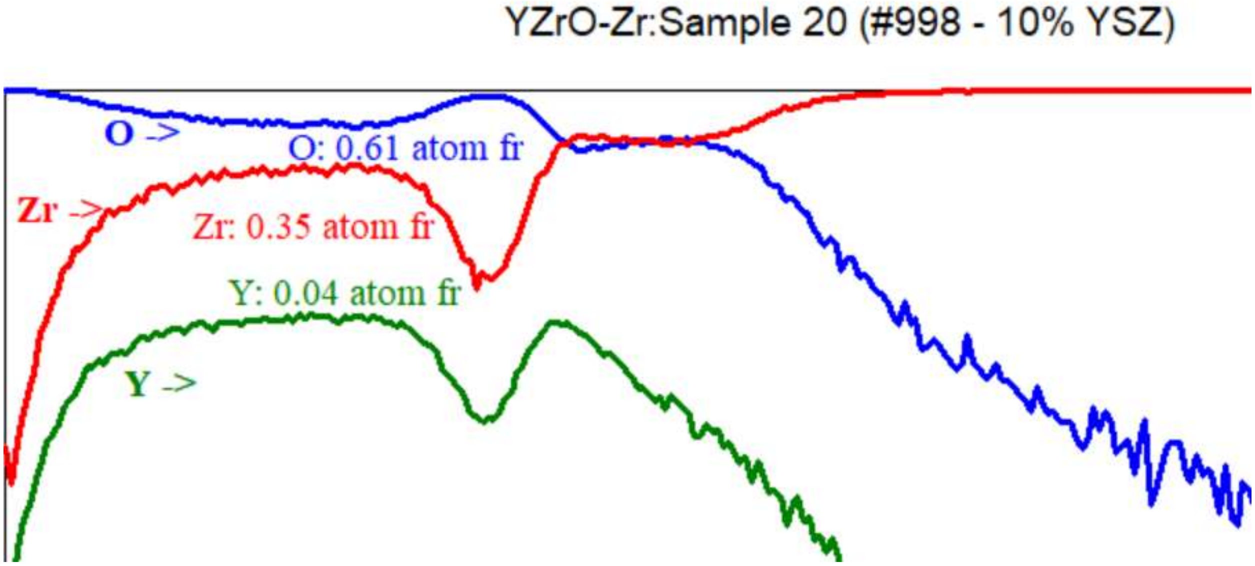


Figure 15: SIMS data set to XPS values for quantification

Neutralization methods for insulating samples

Samples for SIMS analysis must be conducting enough to get a proper secondary ion signal. Some samples are insulating enough that they need some way to stop the sample from holding a charge. This is referred to as "charge neutralization". One simple way to charge neutralize sample that are mildly insulating is to coat them in gold. This allows a clear path to ground through the samples surface and conductive silver paste used to mount the samples. This only works to correct mild charging of a sample. In sample that are more insulating, an electron gun is used to flood the sample with electrons during the analysis. The YZO/Al2O3 samples in this experiment were very insulating. These samples were coated in Au and an electron gun was used during the analysis in order to get adequate secondary ion signal in the depth profile.

Backgrounds vs Detection limit

In SIMS, the terms “backgrounds” and “detection limits” are used frequently. The “backgrounds” are the ambient levels of any element within the SIMS instrument. Ideally, the background levels of an element are lower than the detection limit of the SIMS instrument and so the low background levels of an element will not interfere with the measurement of said element at low concentrations. In some cases, however with atmospheric elements like oxygen and hydrogen, there can be low levels in the SIMS instrument that prevent a true detection limit from being reached.

Analysis conditions

In this experiment, the SIMS data was taken on the PHI Adept 1010 SIMS instrument. The base pressure in the instrument is ~6E-11 Torr. The main YZO compositional analyses were performed with a primary ion beam energy of 2.5keV and a primary ion beam current of ~30nA. The area for analysis was ~500 square microns. (rastered area of primary ion beam) The gated area used was 15%. This relatively large gating was used because the SIMS sputter area was rather large at 500um, so crater edge artifacts were not a concern. The other reason was because these YZO films are thin. Because these films are thin, the analysis had to be tailored to sputter slower through the film in order to get sufficient data density. The primary ion current was chosen to sputter slowly through the film. The trade off for sputtering slowly is that there is less secondary ion signal. More current in the SIMS primary ion beam will yield more secondary ion signal. Larger gating was picked to allow more signal to pass into the analyzer, making up for the signal lost from sputter speed. The analyzer was set up to look at positive ions. To further help improve secondary ion signal intensity, molecular masses were monitored for each element in the form of cesium plus the mass of the element of choice. (133 + X) A compositional measurement was taken on each sample. In the following, we will discuss the compositional results of the SIMS data taken on each sample and draw some conclusions and correlations between growth temperatures, growth duration and substrates used.

YZO on Si

There were six YZO films deposited onto Si substrates. They were targeted at 1% Yttrium, 3%, 5%, 7%, 8% and 10%. Below are the composition SIMS data for each film. (log scale)

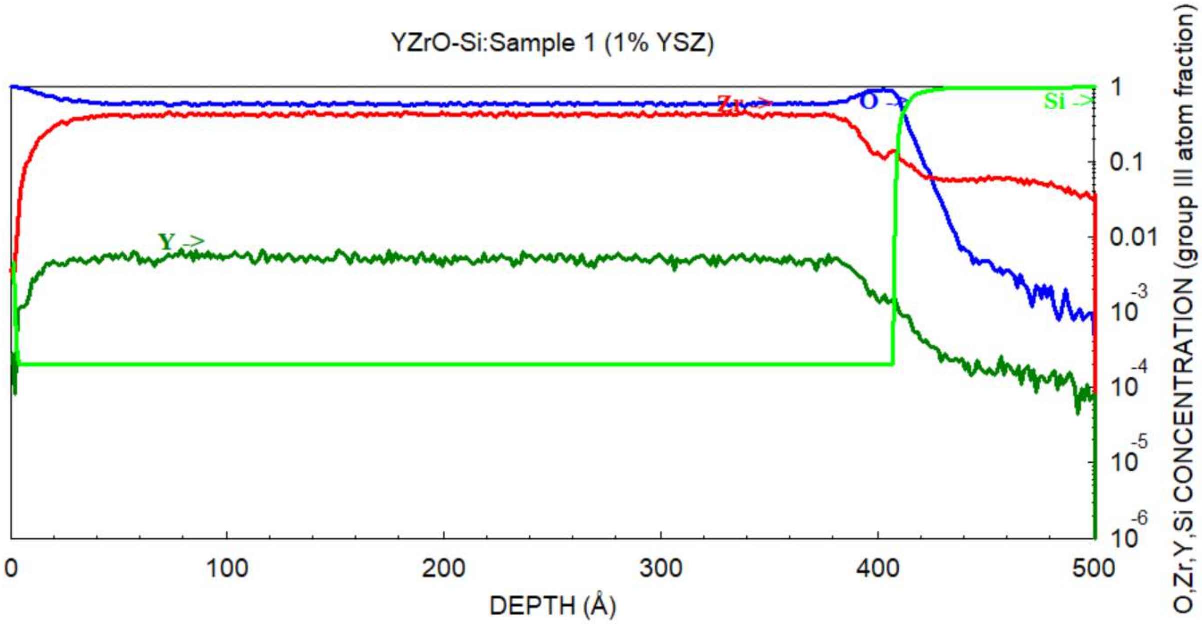


Figure 16: Composition depth profile of 1% Yttrium YZO film on Si

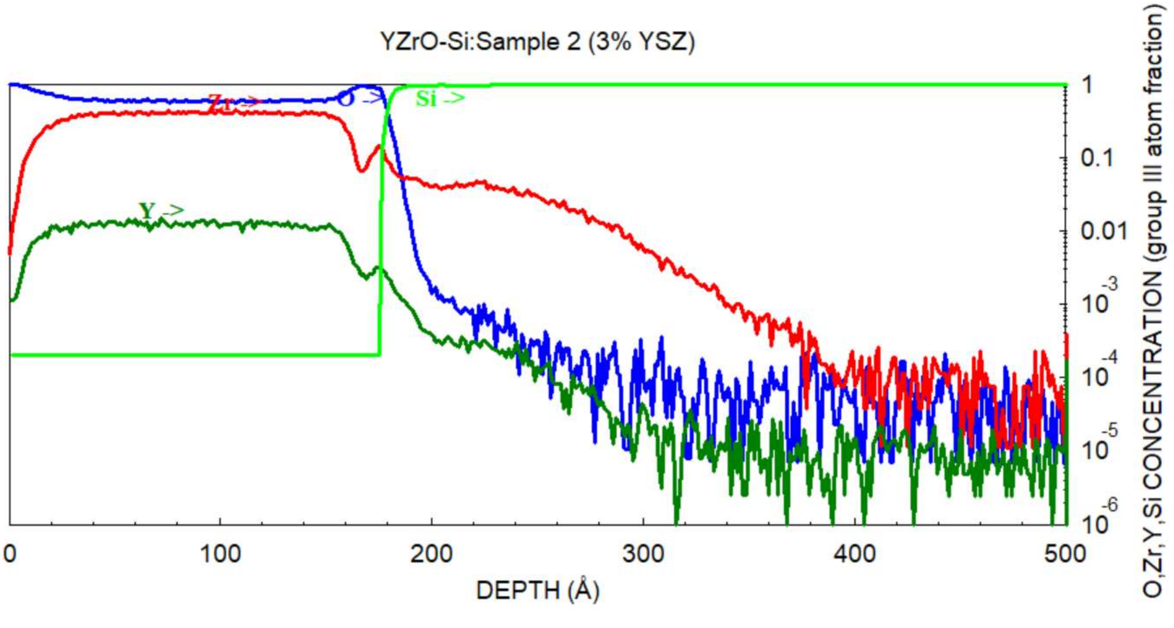


Figure 17: Composition depth profile of 3% Yttrium YZO film on Si

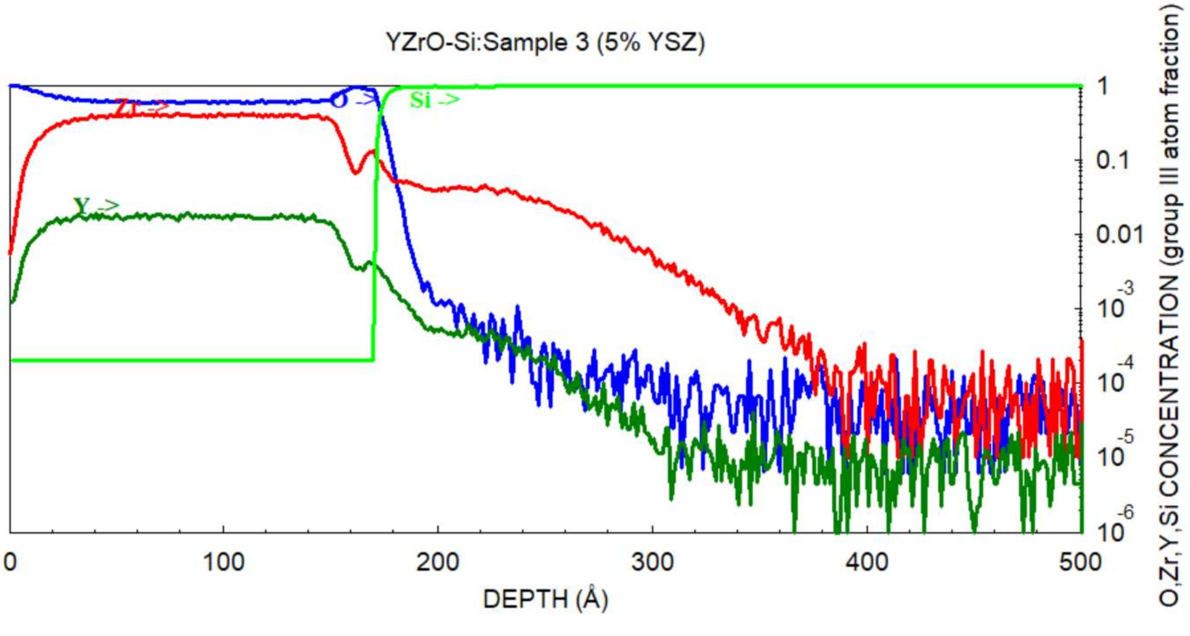


Figure 18: Composition depth profile of 5% Yttrium YZO film on Si

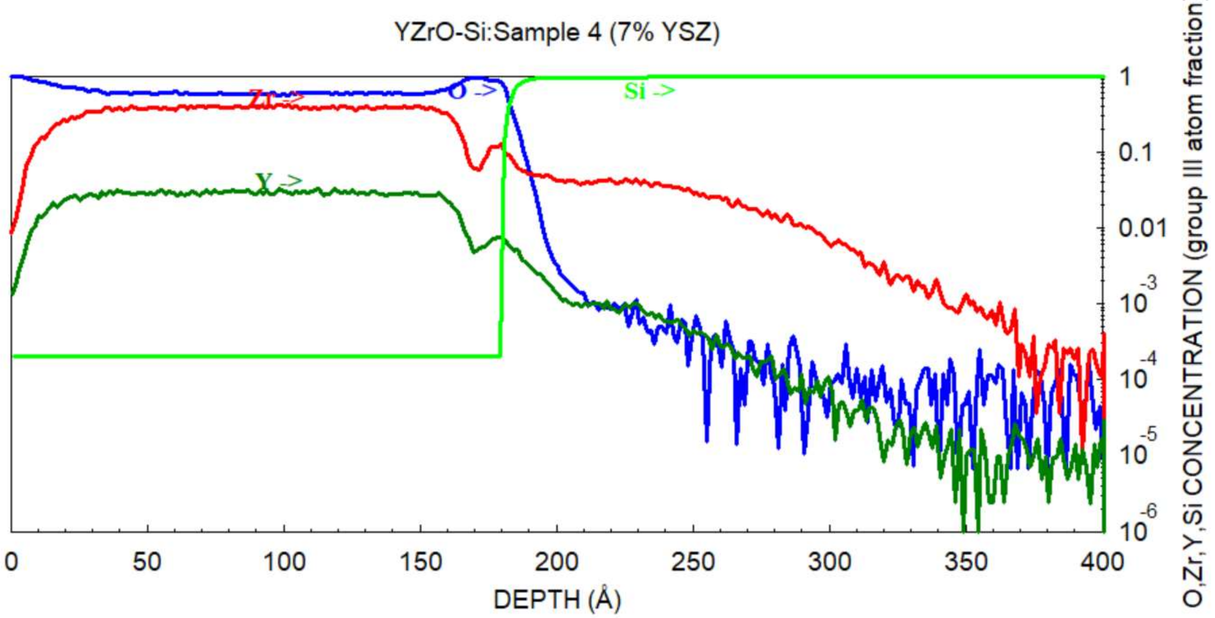


Figure 19: Composition depth profile of 7% Yttrium YZO film on Si

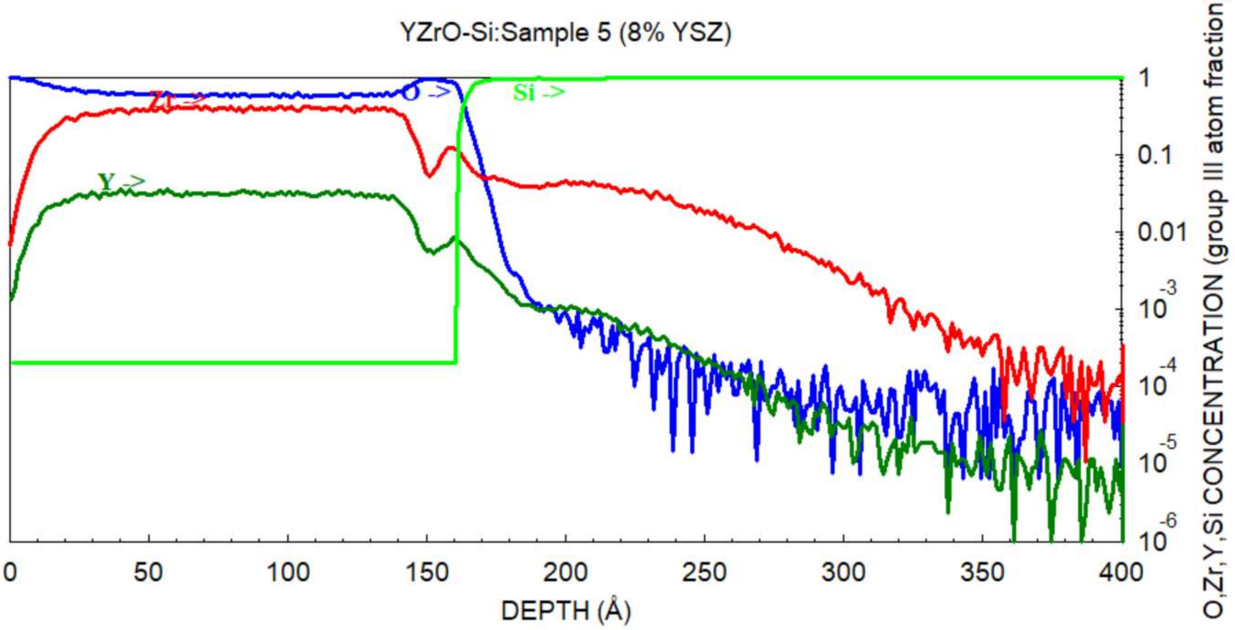


Figure 20: Composition depth profile of 8% Yttrium YZO film on Si

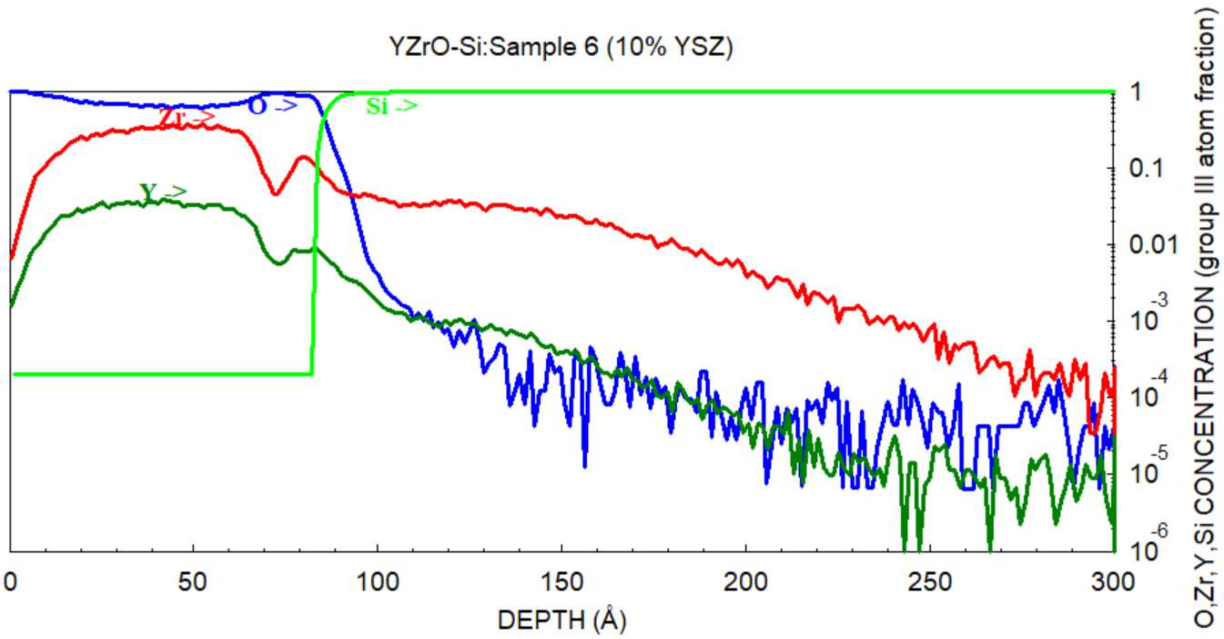


Figure 21: Composition depth profile of 10% Yttrium YZO film on Si

Evaluation of YZO on Si

A comparison of the sample shows the general trend in Yttrium content and demonstrates good agreement with the intended results. The measure percentage of Yttrium deviates from the expected value. (i.e. the 1% Yttrium sample is measured to have closer to 4.4% Yttrium) This is likely due to a combination of factors. The actual targets made for the PLD growth can have an error associated with them, as the elements are being hand measured and pressed into pellet form. The process of PLD grown is not done at ultrahigh vacuum, so there can be contaminants that were not measured during the XPS quantification of the films. If this contamination is at the percent level, it will begin to affect the composition of the YZO films. The overall percentage level of the Yttrium is not so important here, as the goal is to evaluate the varying amount of Yttrium in these films and what effects it has on the film.

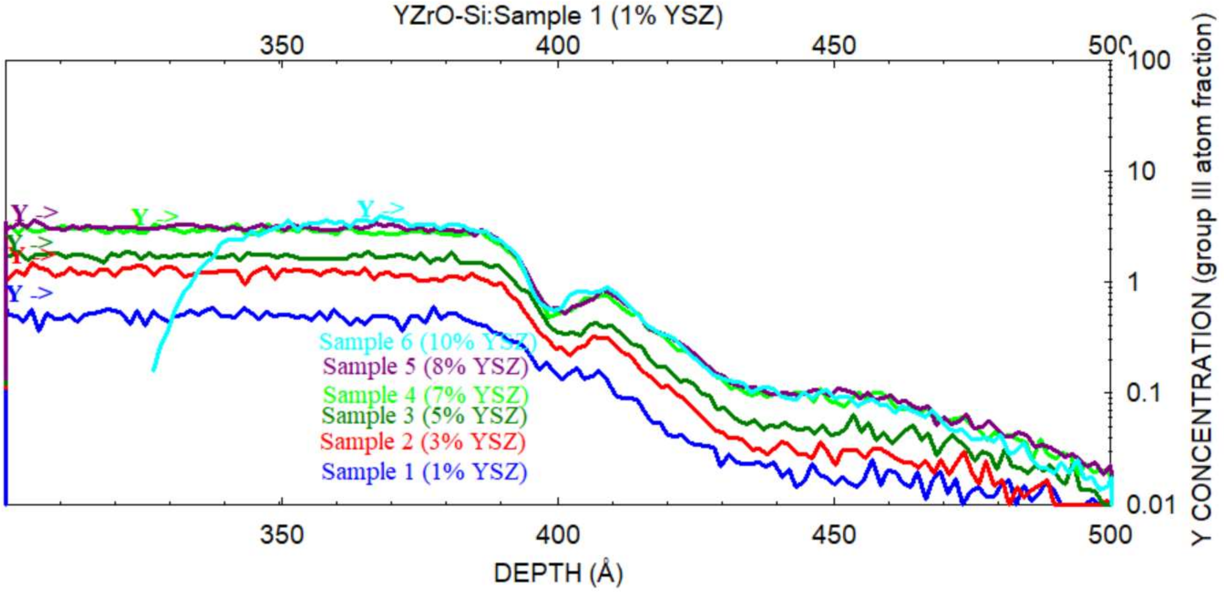


Figure 22: Comparison of Yttrium content in all films grown on Si

The results showed agreement in the trend of Yttrium with respect to the goal amount of Yttrium in the samples. A closer look at the data shows some other interesting features that may give more information about the samples and the film growth.

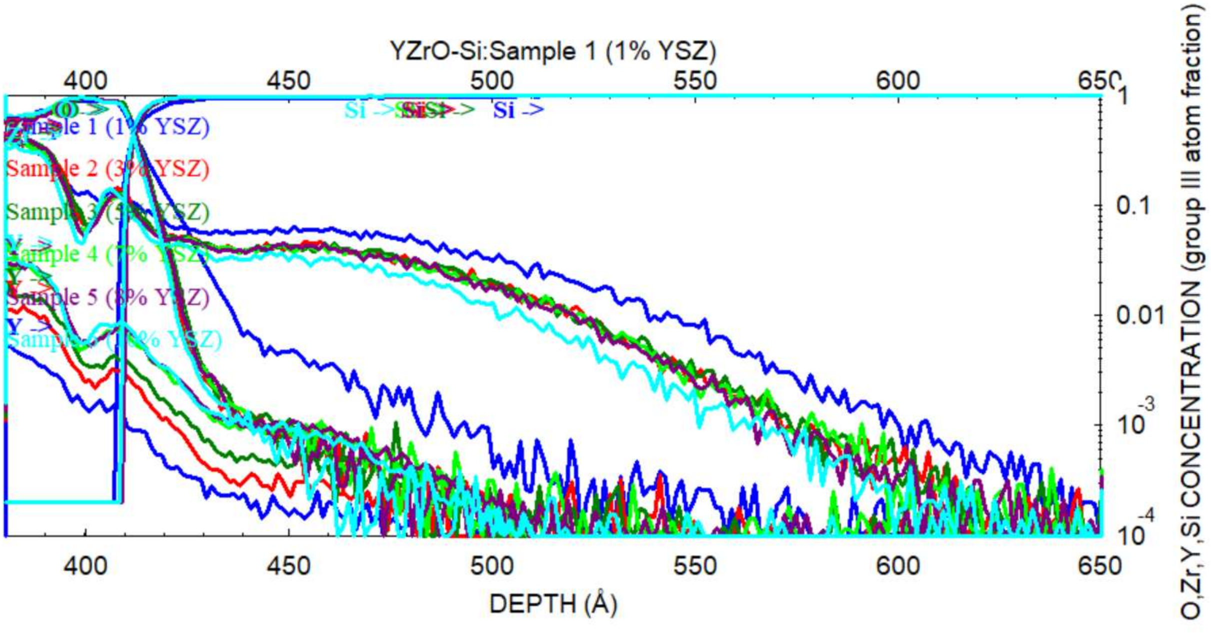


Figure 23: Evidence of surface roughness at substrate interface in films grown on Si

Sample roughness

The samples all showed some amount of roughness. This can be seen in the SIMS data as the “tails” of the profiles at the film/substrate interface. The “tailing” has a slope that arches out before dropping in intensity. This is a typical SIMS artifact from roughness, and more specifically conformal roughening. The roughness here is likely surface roughness that is being worsened as the SIMS primary ion beam sputters through the YZO film. The “conformal roughening” happens when there is a transition between two materials or layers of different roughness. As the SIMS primary ion beam is sputtering through the interface, the film roughness is at its worse (from sputtering on top of being rough to start with), while the Si substrate is very smooth. There is a transition from very rough to very smooth happening that is causing the “tailing” to have “shoulder” to it. We will see that the other substrates of Zr and Al2O3, do not show this feature to the same extent. These substrates have more surface roughness then the Si substrate does, so the “tailing” we see in the data from those samples shows more typical surface roughness artifacts and less of this “conformal roughening”.

Substrate interface

The substrate interface is another area where the SIMS data can give us information about the films.

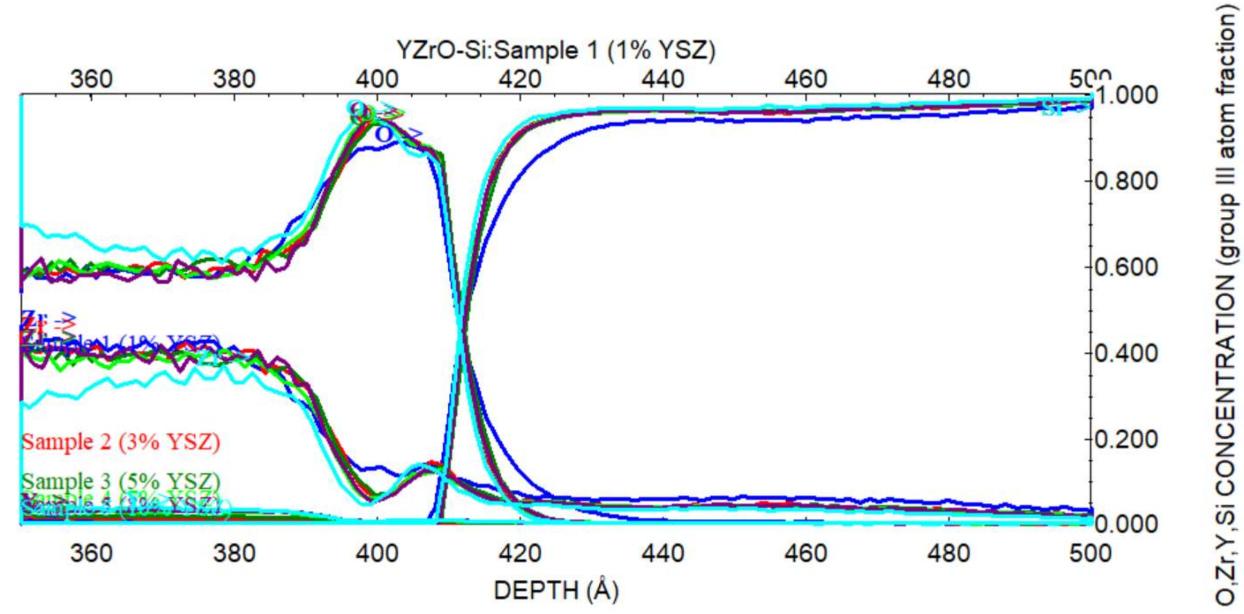


Figure 24: Comparison of substrate interface of all films grown on Si (Linear scale)

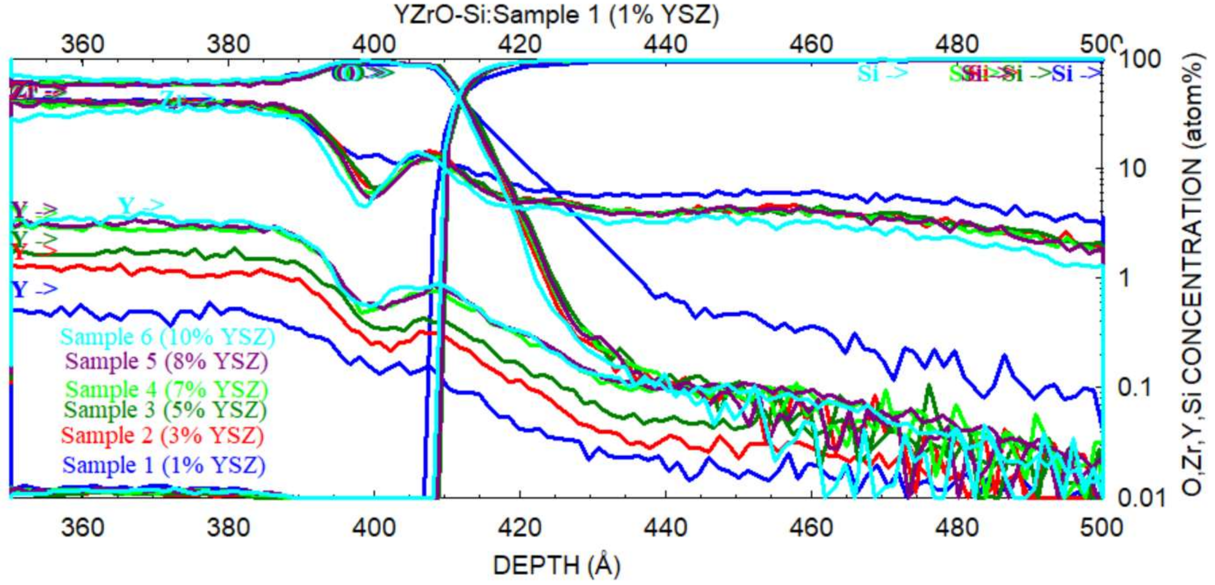


Figure 25: Comparison of substrate interface of all films grown on Si (Log scale)

The substrate interface of the films on Si substates shows there was a surface oxide on the substrate at the time of growth. It also shows that some of the Yttrium and Zirconium have migrated to the substrate interface. The increase in Zr and Y after the intensity drops in the surface oxide of the substrate could be evidence of migration during the growth process. This is likely not a SIMS artifact, as an increase in intensity is typically only an artifact if there is a mass interference or if there is some normalization artifact. The mass interference artifact could be plausible here, as three mass 30 isotopes of Si can interfere with Zr, however we would continue to see that interference in the substrate, and we do not. A normalization artifact can happen when the signal being normalized to dip significantly in intensity while the element being normalized does not. Here, that has not happened, as even the raw, unnormalized data show the same feature at the Si substrate interface.

YZO on Zr

There were seven YZO films grown on zirconium substrates. The films had the same variation of Yttrium as the set of films on Si substrates (1%, 3%, 5%, 7%, 8% and 10%), however there were two films grown with 10% Yttrium in this set of samples. Below are the composition SIMS data for the YZO films on Zr substrates.

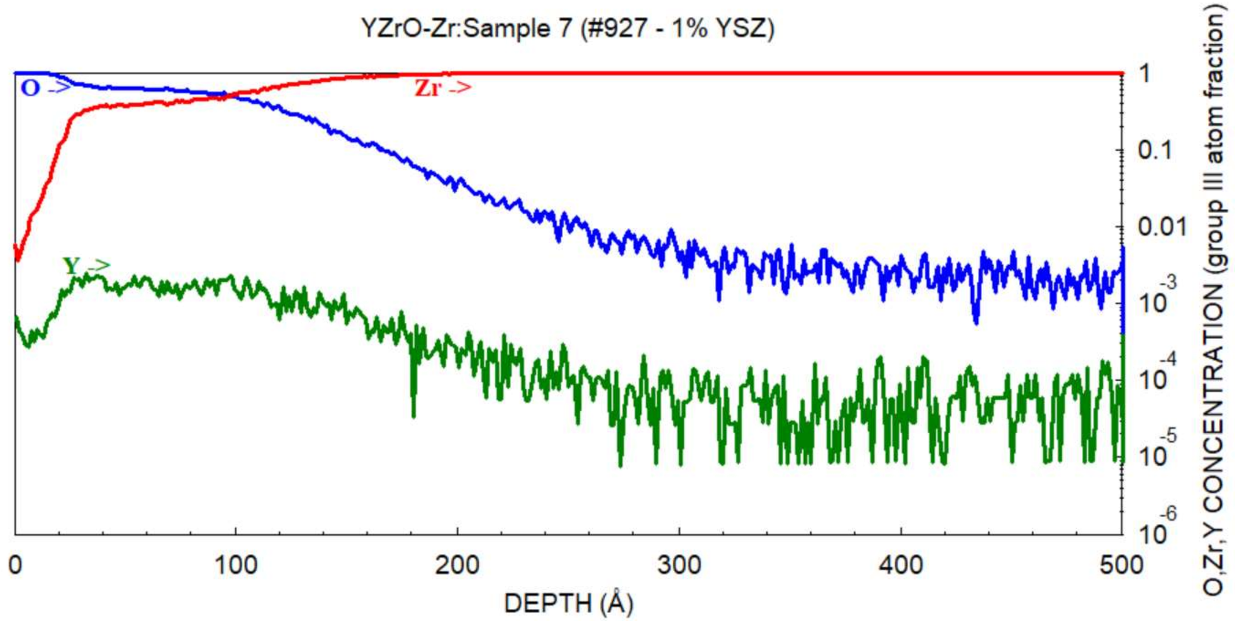


Figure 26: Composition depth profile of 1% Yttrium YZO film on Zr

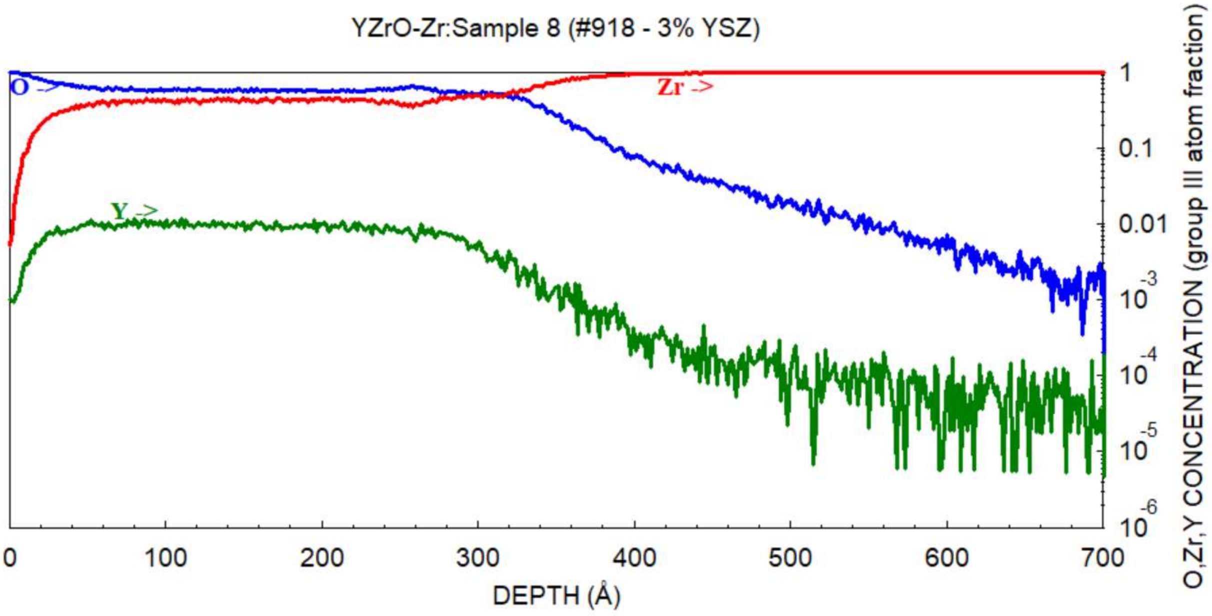


Figure 27: Composition depth profile of 3% Yttrium YZO film on Zr

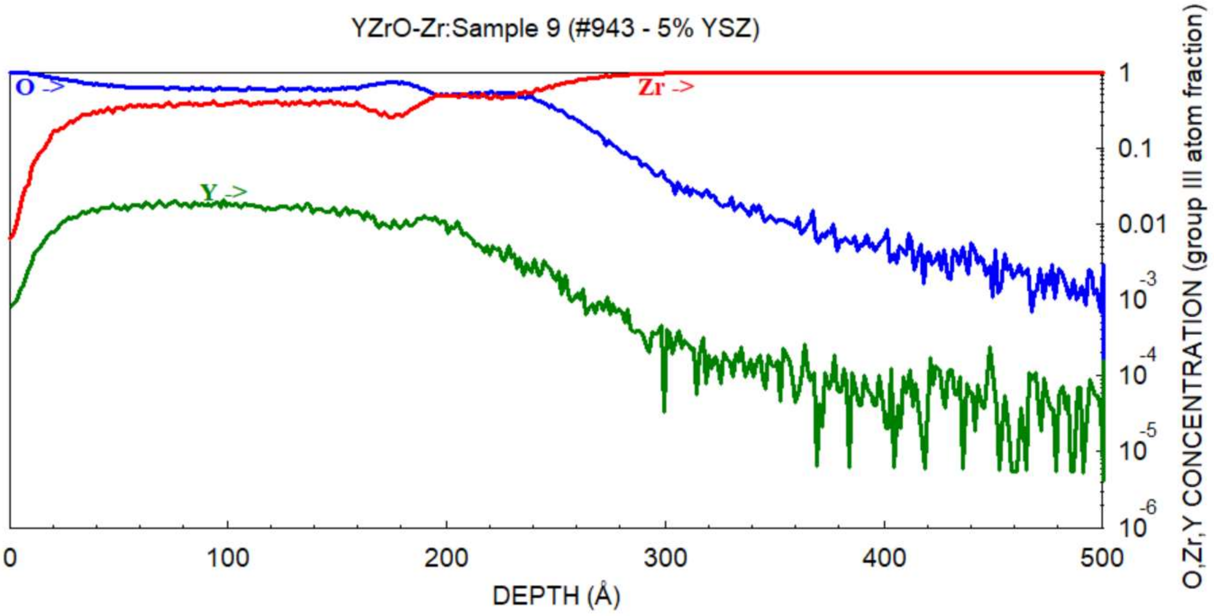


Figure 28: Composition depth profile of 5% Yttrium YZO film on Zr

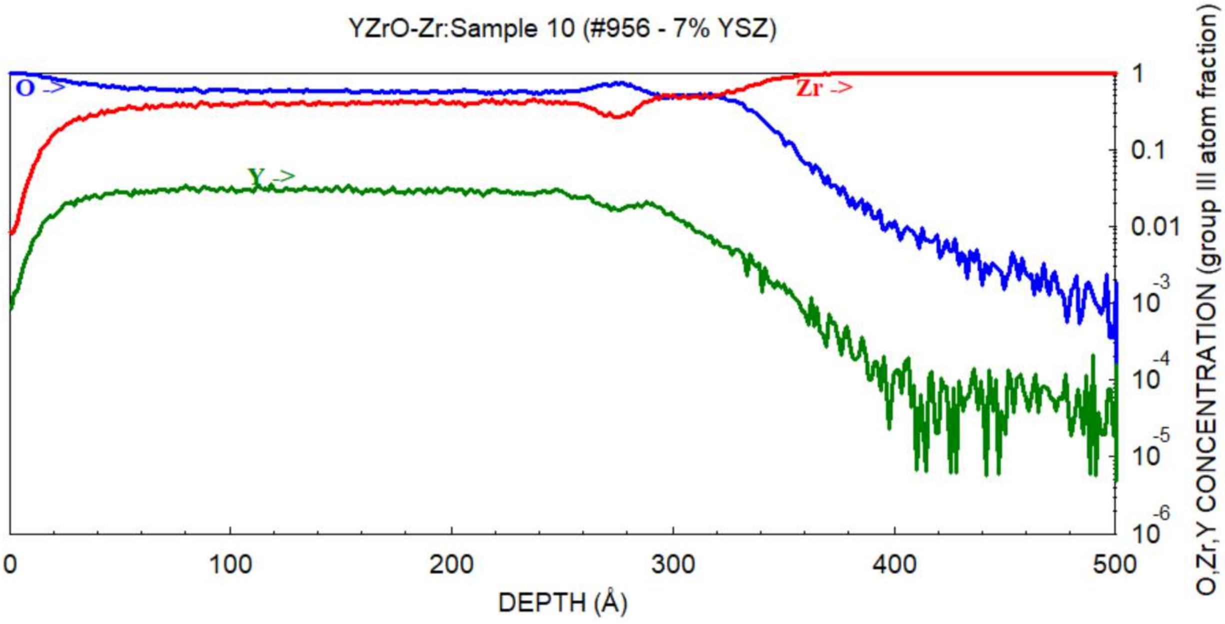


Figure 29: Composition depth profile of 7% Yttrium YZO film on Zr

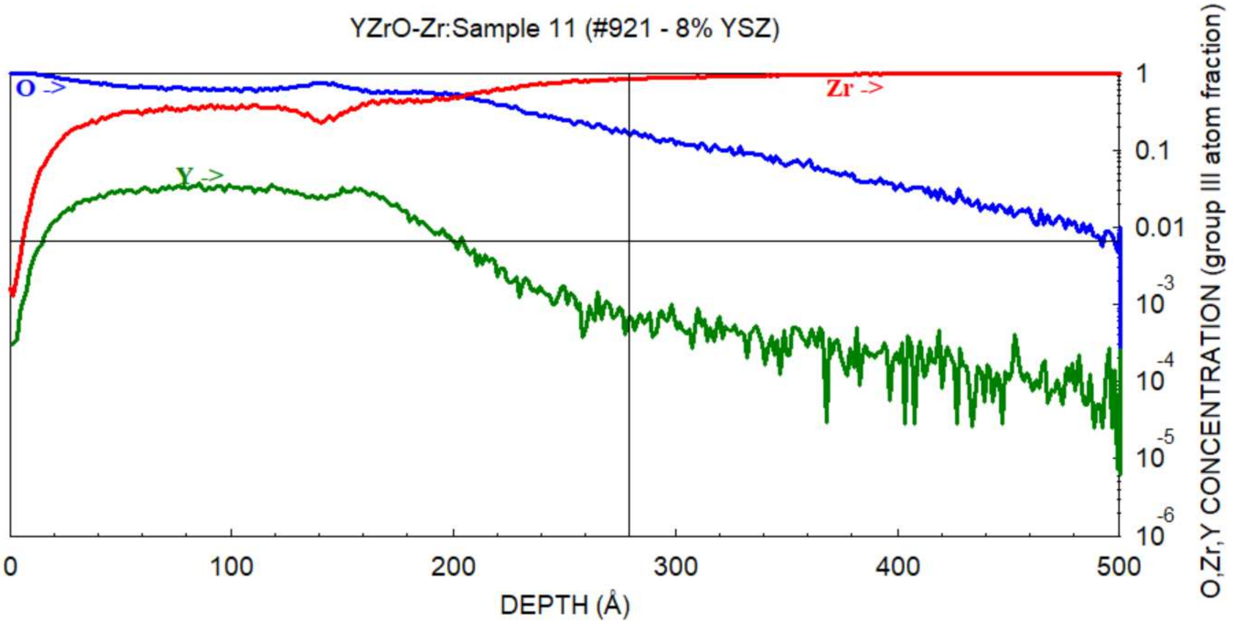


Figure 30: Composition depth profile of 8% Yttrium YZO film on Zr

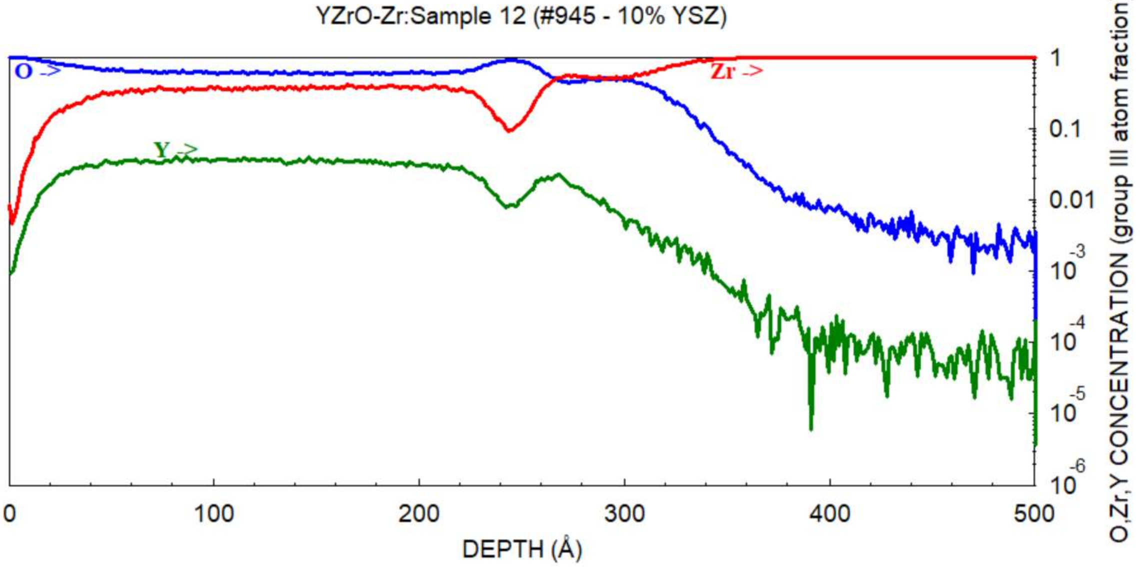


Figure 31: Composition depth profile of 10% Yttrium YZO film on Zr

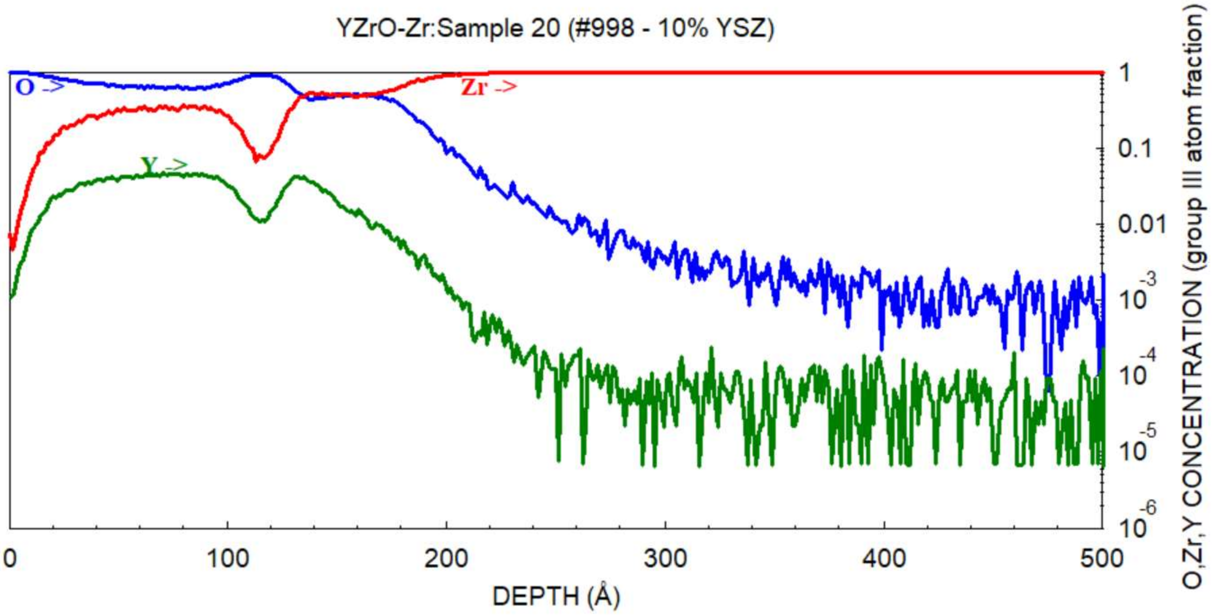


Figure 32: Composition depth profile of 10% Yttrium YZO film on Zr

Comparison of YZO on Zr

Here again, we compare the composition SIMS data and see the general trend of Yttrium agrees well with the theoretical "goal" values for Yttrium for the film growth. Like the films on Si substrate, the absolute values are a bit off from the intended values of Yttrium incorporation, but as explained earlier, that is to be expected for a few reasons discussed above.

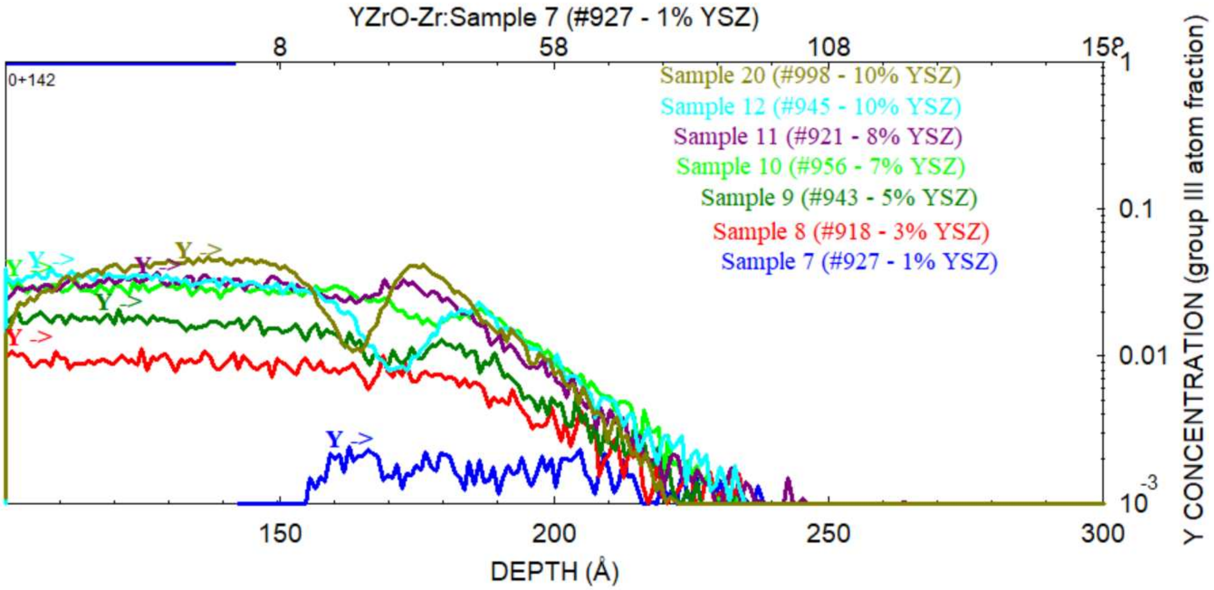


Figure 33: Comparison of Yttrium content in all films grown on Zr

Substrate interface

In looking at the substrate interface between the samples, we see that there appears to be a region of ZrO followed by a thin oxide before the YZO film starts. This is seen more so on the films with higher levels of Yttrium. This result is perplexing, as one would not expect to see this as a function of Yttrium content. This ZrO layer could also just be a product of the substrates themselves having a thick oxide on them, resulting in Ox diffusion into the Zr substrate during the film growth. This would also explain the thin purer Oxide above the ZrO layer. That said, there is some Yttria seen just below the Oxide at the ZrO/Oxide interface. This might mean there is some additional diffusion going on during the growth process.

There is some "tailing" into Zr seen in these films at the substrate interface. Sample 11 for example shows significant Ox tailing into the substrate, while others show a sharper interface. Sample 11 may have had a rougher surface that would yield this type of tailing in the SIMS depth profile. This tailing could also be from actual Ox contamination in the substrate, but this seems unlikely given the sharpness of the other films at the substrate. Energetic contamination from the cesium primary ion beam can cause this type of "knock in" effect that will look like this Ox tail, however the primary ion beam used here was a low enough energy, one would not expect this type of SIMS artifact. Additionally, one would see this in the other profiles of the same film and in the other films if this were a SIMS artifact from the primary ion beam. The slope of the decreasing Ox does not match the Yttrium, so the cause of this is sample related and not from the SIMS.

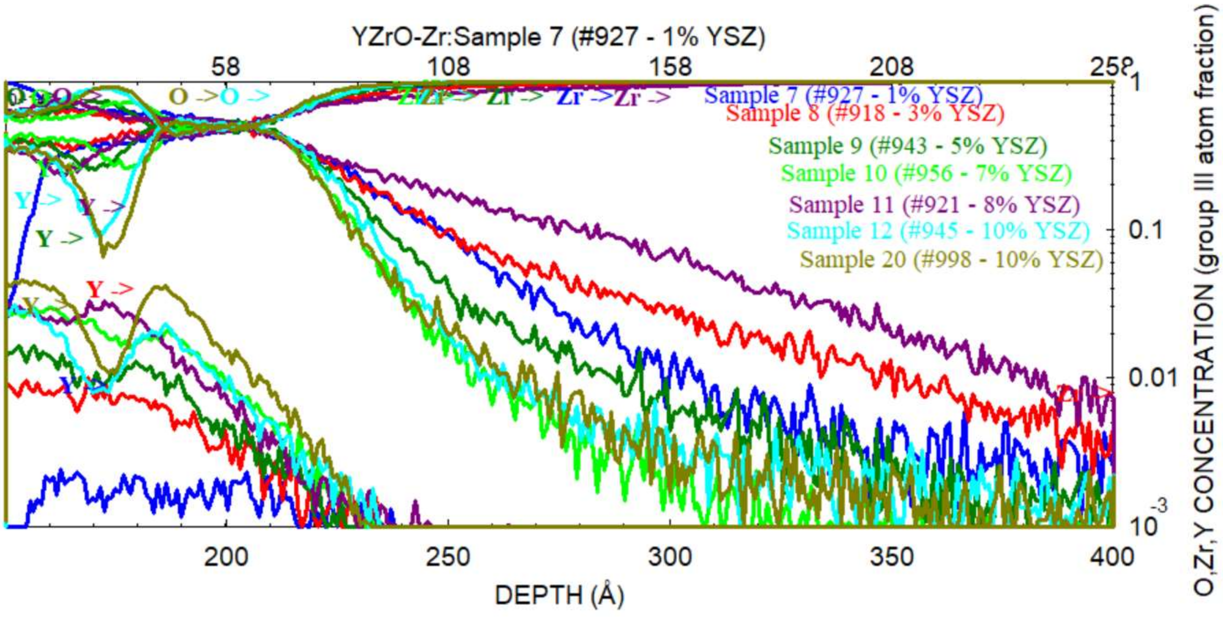


Figure 34: Comparison of substrate interface of all films grown on Zr (Log scale)

On a linear scale some of these interface features are more obvious. On a linear scale, one can see the gradual slope of Zr going into the substrate on sample 11 matches the gradual slope of the Ox tailing down into the substrate. This suggests that roughness is the reason for this tailing artifact. Further tests are needed to evaluate the surface roughness of this sample when compared to the other sample in this set of Zr substrates.

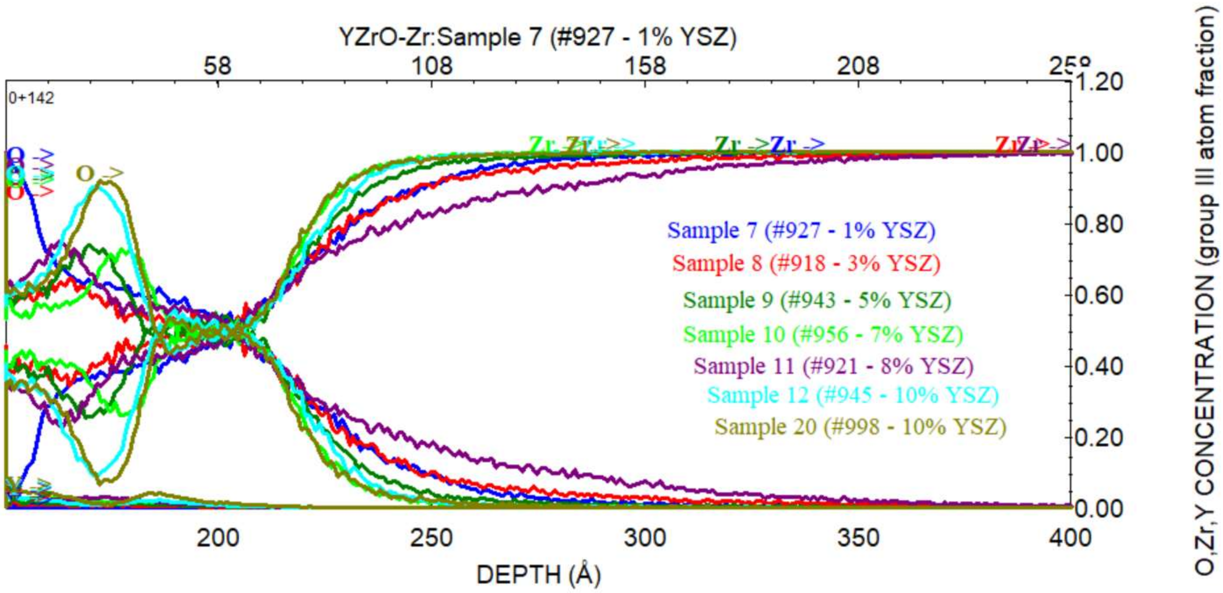


Figure 35: Comparison of substrate interface of all films grown on Zr (Linear scale)

YZO on Al2O3

There were seven YZO films grown on alumina substrates. The films had the same variation of Yttrium as the set of films on Si substrates (1%, 3%, 5%, 7%, 8% and 10%), however there were two films grown with 10% Yttrium in this set of samples. Below are the composition SIMS data for the YZO films on Al2O3 substrates.

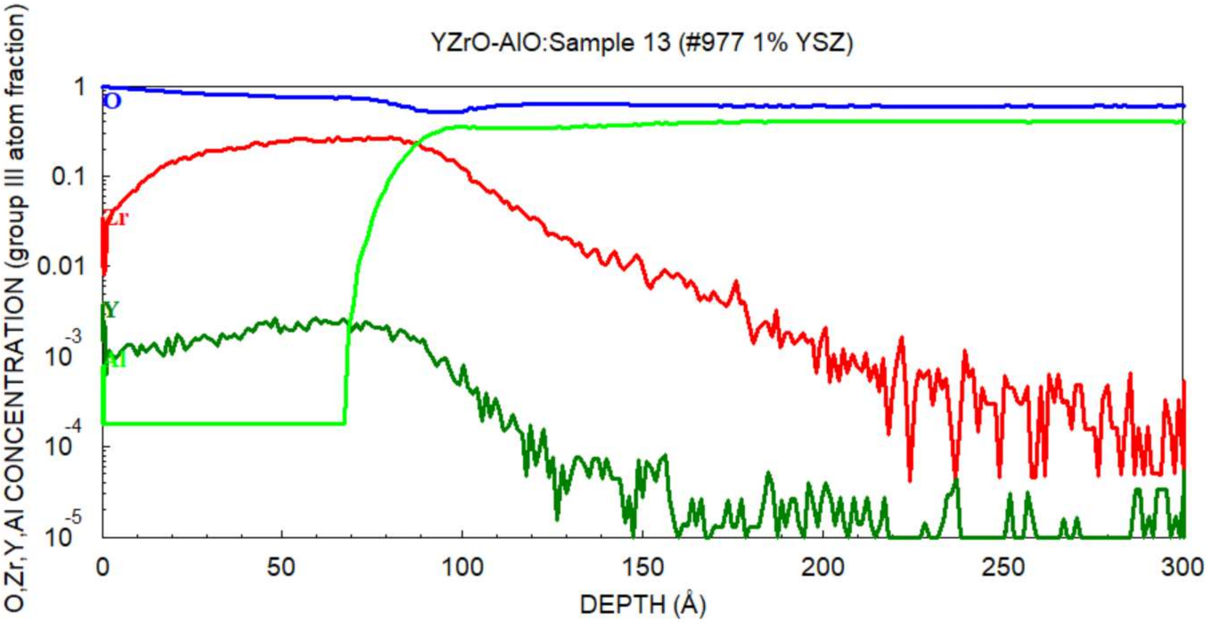


Figure 36: Composition depth profile of 1% Yttrium YZO film on Al2O3

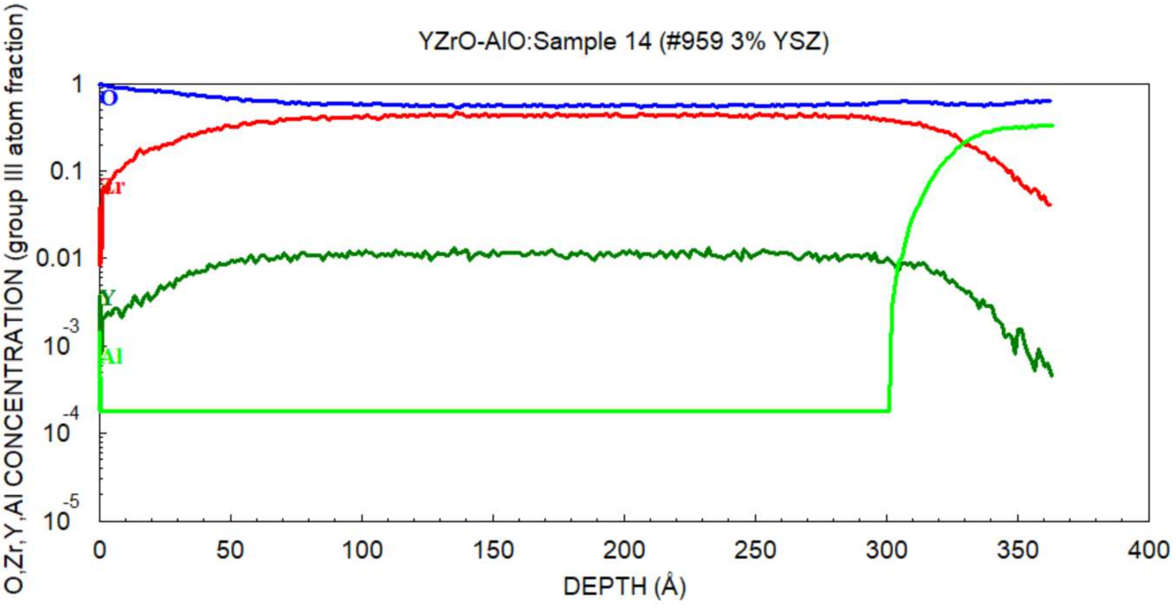


Figure 37: Composition depth profile of 3% Yttrium YZO film on Al2O3

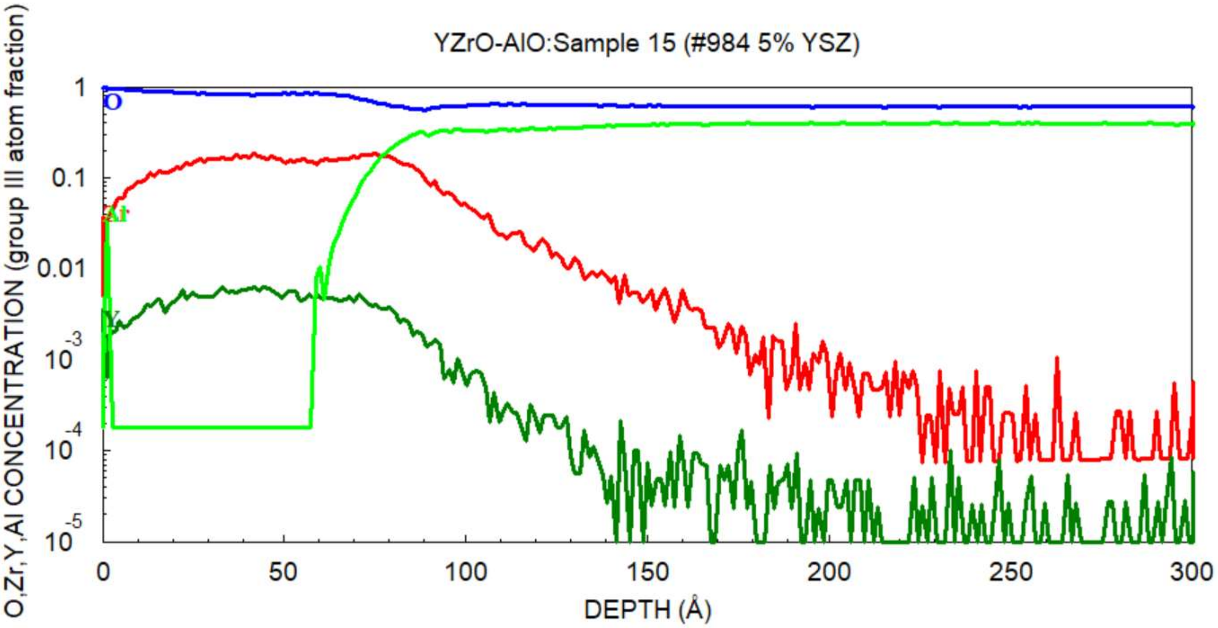


Figure 38: Composition depth profile of 5% Yttrium YZO film on Al2O3

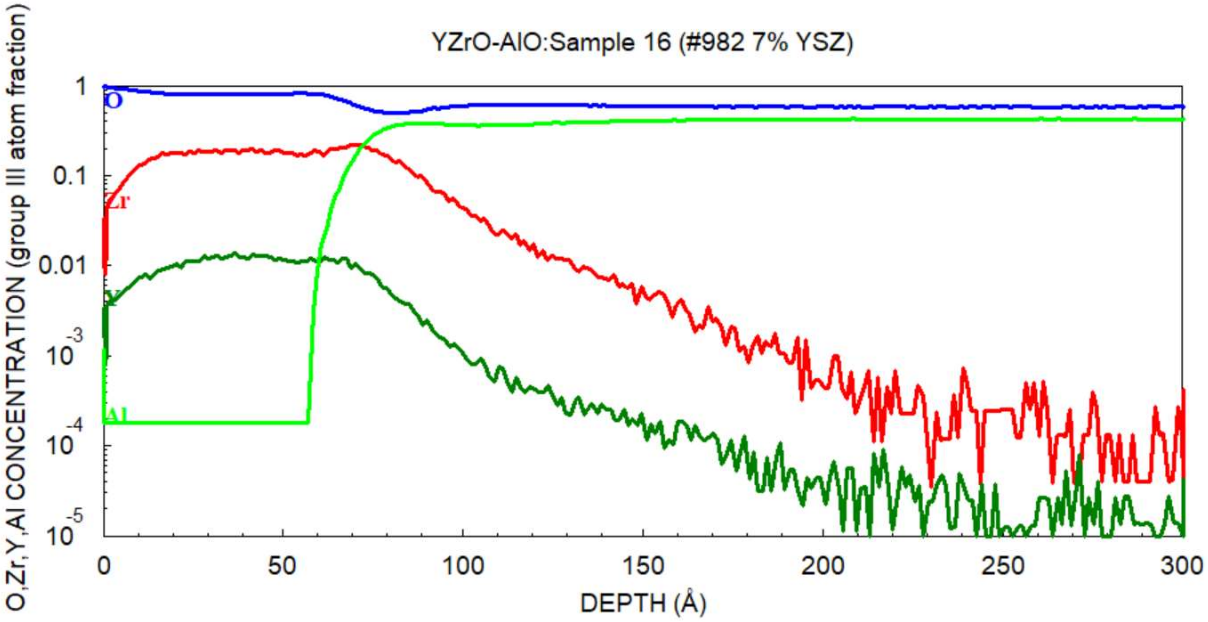


Figure 39: Composition depth profile of 7% Yttrium YZO film on Al2O3

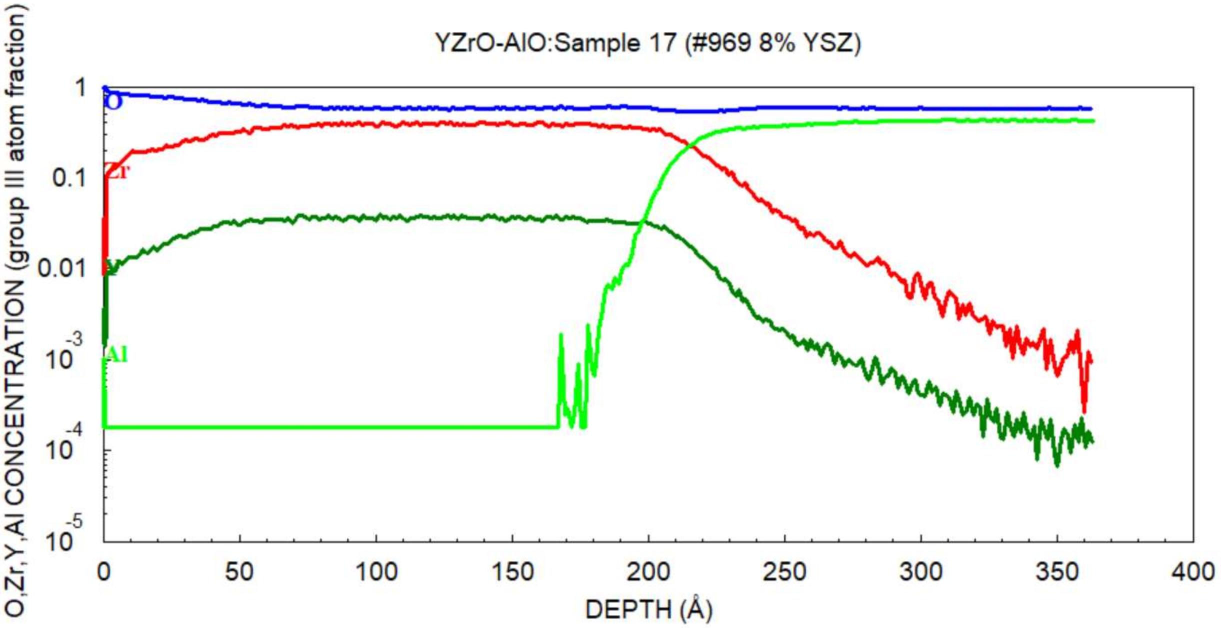


Figure 40: Composition depth profile of 8% Yttrium YZO film on Al2O3

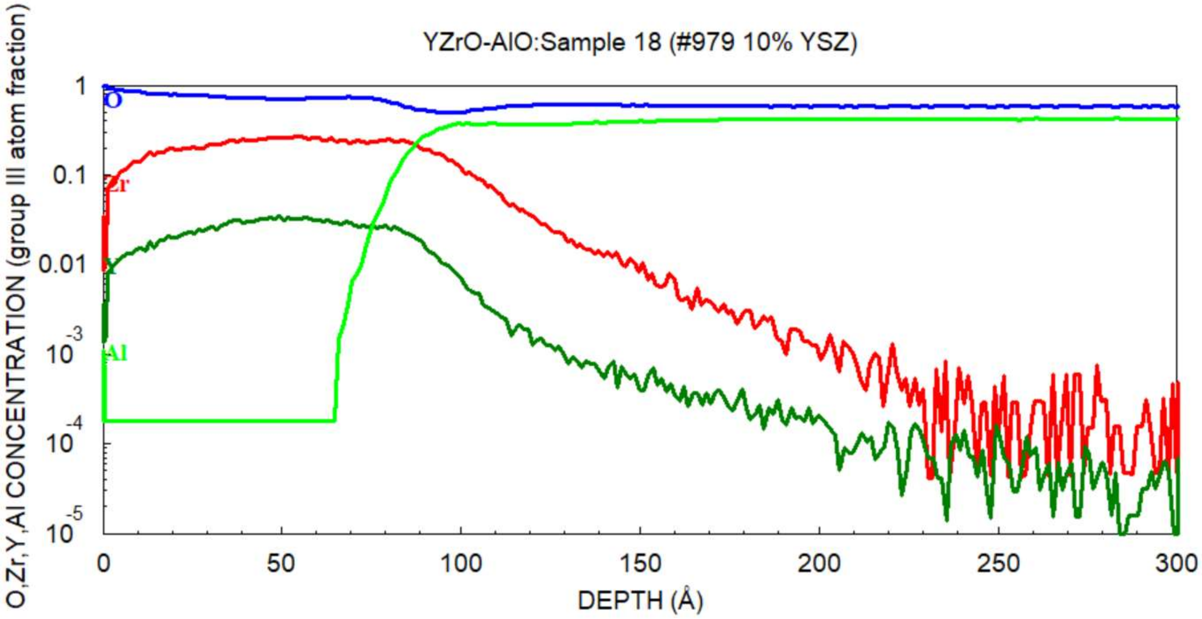


Figure 41: Composition depth profile of 10% Yttrium YZO film on Al2O3

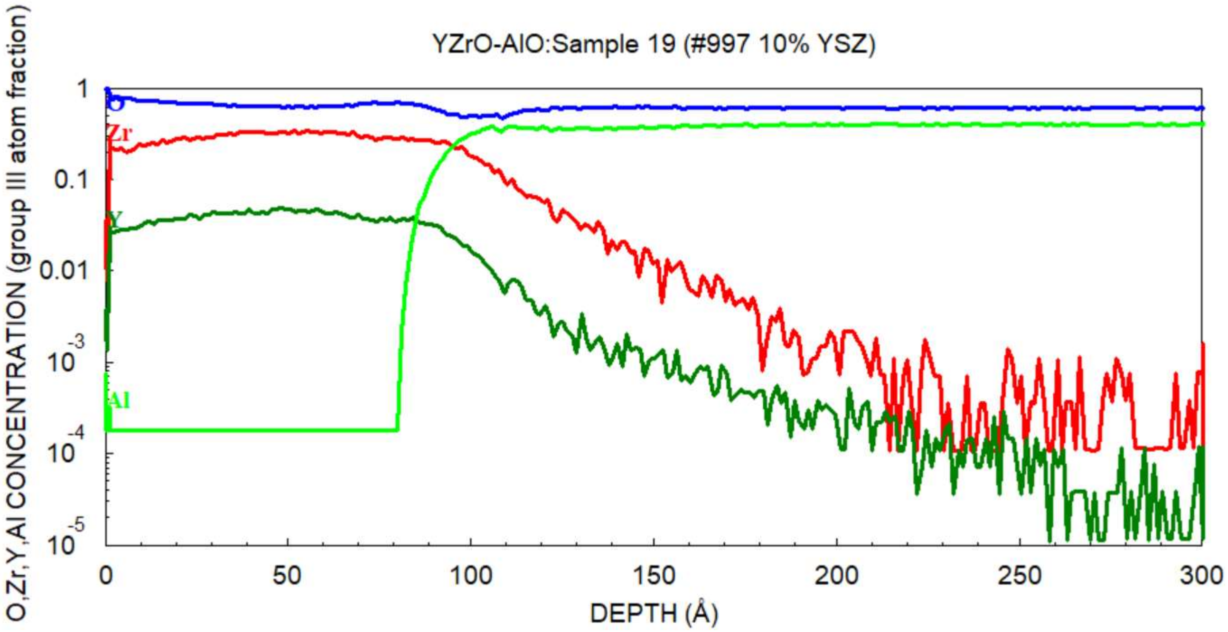


Figure 42: Composition depth profile of 10% Yttrium YZO film on Al2O3

Comparison of YZO on Al2O3

The trend in Yttrium content is generally the same as the other substrates in that it is lower than the target value but shows the intended increase of Yttrium with each successive sample. This set of samples, however, was not as close in scale to the intended increase of Yttrium. There was a discrepancy in the 3% sample vs 5% sample where the 3% Yttrium sample showed higher Yttrium content then the sample with the 5% inclusion goal. Additionally, the sample with a goal of 8% Yttrium inclusion was seen to have similar Yttrium content as the two samples with the goal of 10% Yttrium inclusion. It is difficult to diagnose why this happened in this batch of samples. This likely has nothing to do with the substrates in this batch of samples and is related to the sample growth process itself. One possibility of how this could happen could be human error in the PLD target making process or in the growth conditions of the PLD instrument. If the same set of targets were used for all substrates, then this could be a sign of nonuniformity in the targets themselves.

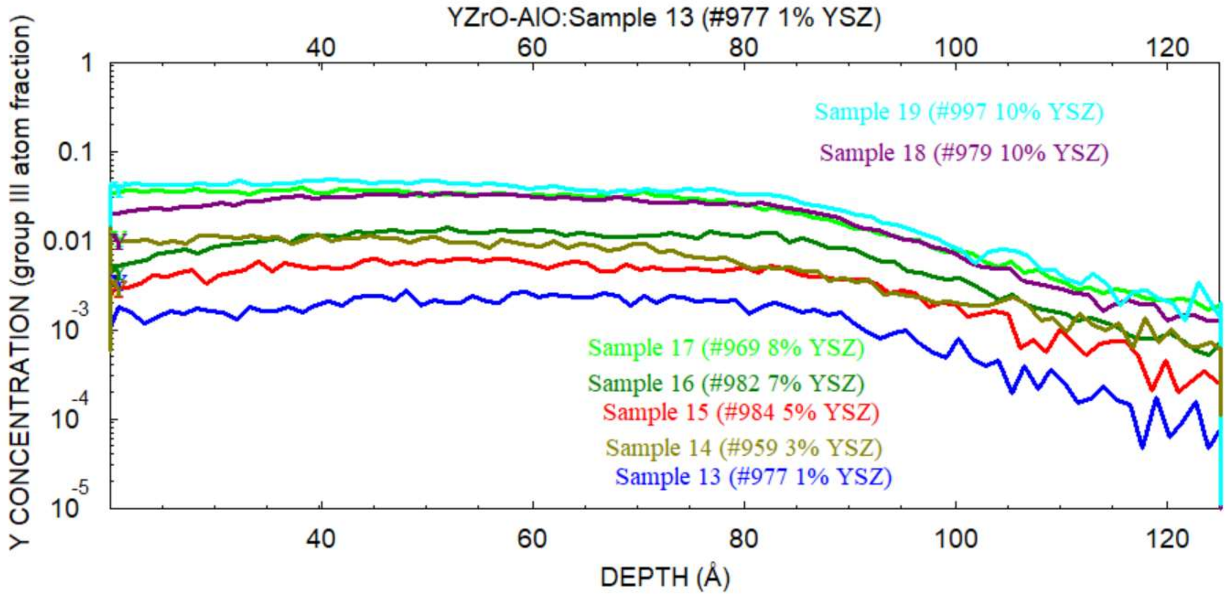


Figure 43: Comparison of Yttrium content in all films grown on Al2O3

Substrate interface

When we compare the substrate interfaces on this batch of samples, we see some secondary shouldering in the Zr and Y “tails” of the profile as they go into the substrate. This could suggest some change in roughness between the YZO film and the Al2O3 substrate (conformal roughening), but we mostly see general broadening of the substrate interface from the surface roughness of the YZO film.

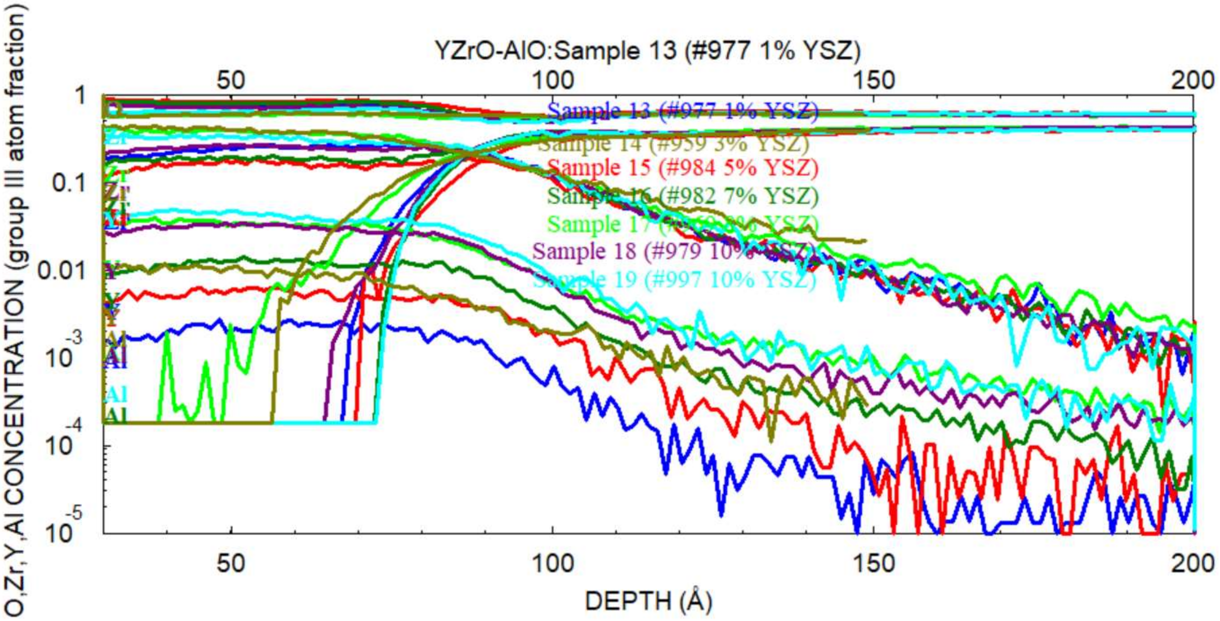


Figure 44: Comparison of substrate interface of all films grown on Al2O3 (Log scale)

Looking at the substrate interface on a linear scale shows there increase in Ox right after growth was started. (Some samples more than others) This is likely related to the surface Oxide that existed on the substrates prior to growth. There doesn't appear to be a correlation between the increase in Ox seen and the Yttrium inclusion amount, as it appears randomly larger in some samples.

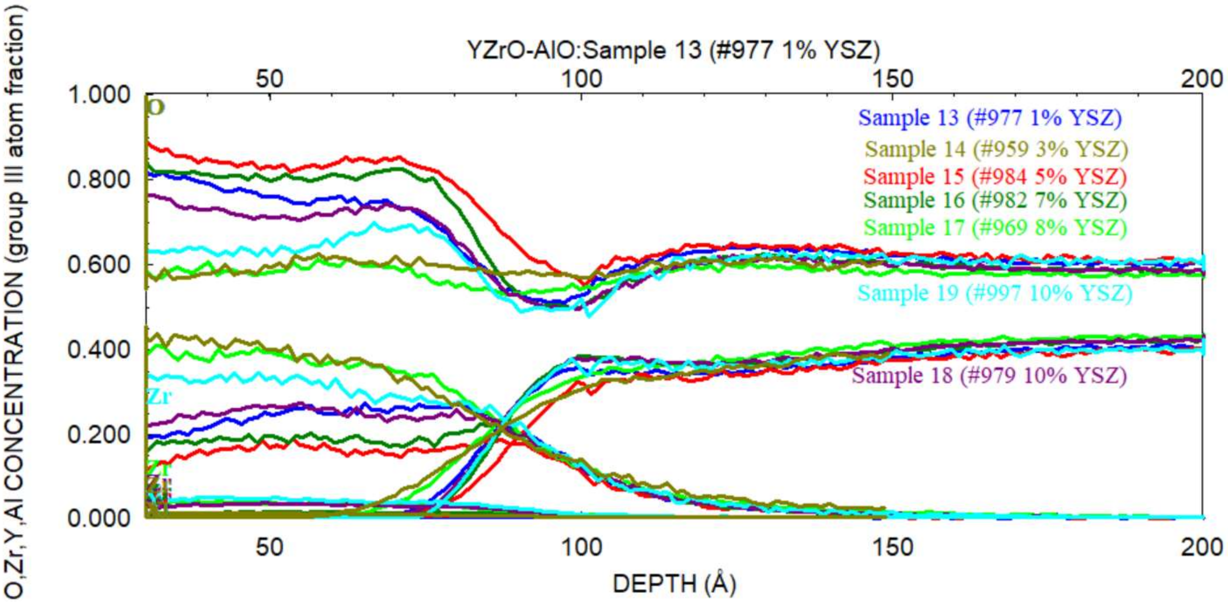


Figure 45: Comparison of substrate interface of all films grown on Al2O3 (Linear scale)

SIMS precision and primary ion beam stability

After the SIMS analysis was complete, a repeat measurement was done on the 3% Yttrium sample from the YZO/Al2O3 batch of samples. This was done to confirm precision of the SIMS data as well as the stability of the primary Cs ion gun current. We see the precision of the SIMS data is excellent and the data come out identical. The primary ion beam current was very stable as well with a drift in current of about 1%. The sputter rate of the initial SIMS profile on this sample was 0.4447 angstroms per second where the repeat analysis had a sputter rate of 0.4400 angstroms per second. This suggests that all film thickness differences seen in the SIMS data are real and not artifacts from primary ion beam current drift. These two measurements were taken very close to each other on the sample, so these results do not shed light on the film uniformity (Thickness or Y content) of the sample.

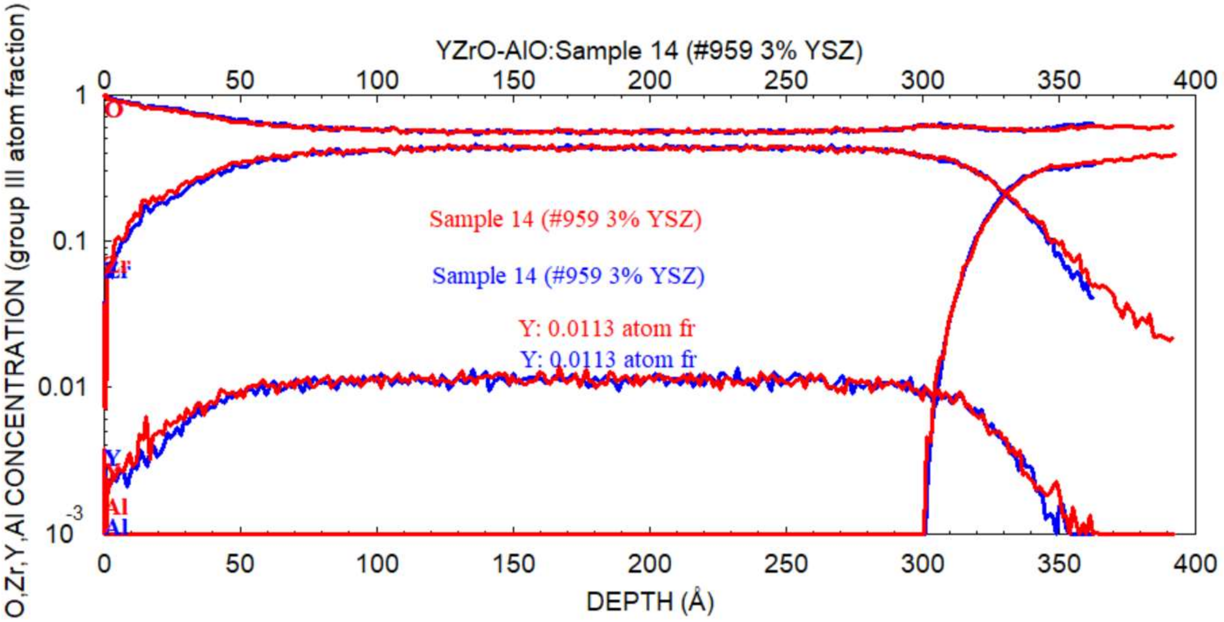
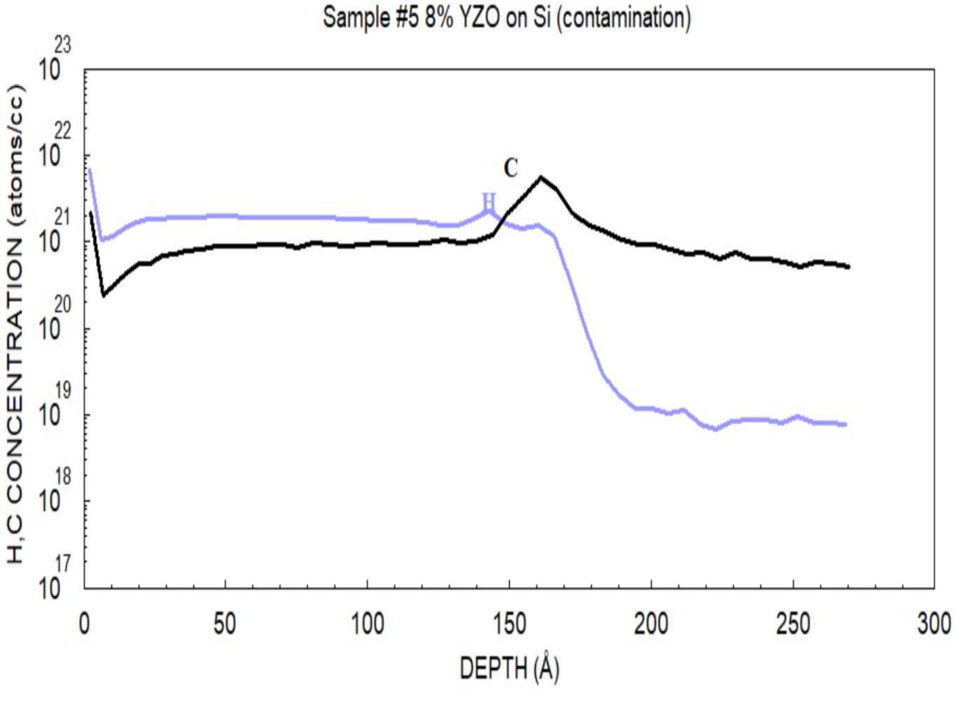


Figure 46: Plot demonstrating SIMS precision of quantification and sputter rate

Impurity measurement

It was seen in the XPS data that there is percent level C in these samples. This prompted us to take a quick contamination profile of a sample from the Si substrate batch and a sample from the Zr substrate batch. We do not have proper reference materials to quantify contaminants in YZO, however we can use archival zirconia reference material data to make an estimate and confirm what was seen in the XPS data.



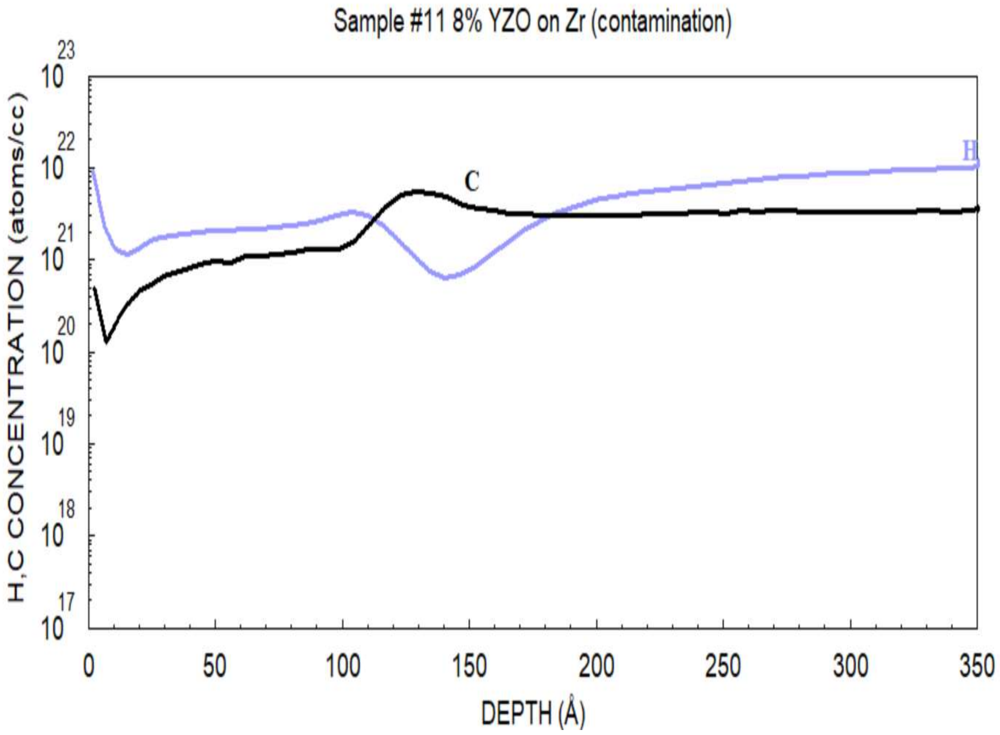


Figure 47: C and H contamination profiles on sample 5 and sample 11

Discussion/conclusion

When we cross examine the SIMS data with the resistivity data in "Experimental Investigation of Surface Resistivity of Yttrium Stabilized Zirconium as a Thin Film" by Matt Melfi, we don't see any strong case in the SIMS as to why the 8% Yttria samples are showing the best conductivity.

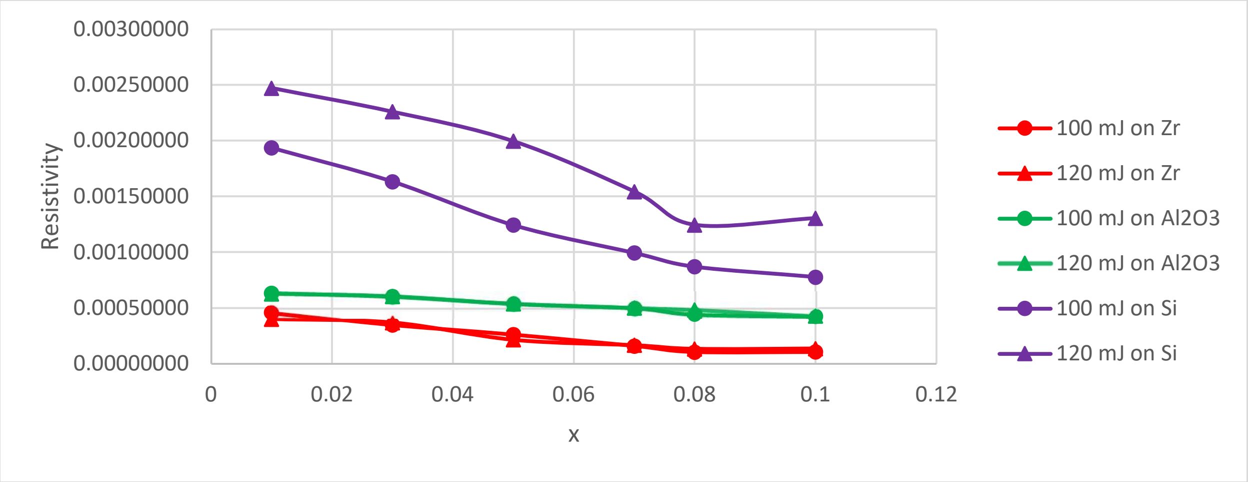


Figure 48: Resistivity results of Polished Zr, Al_2 O_3, Si

In the YZO on Zr samples, we see features that appear more prominent when increasing the Yttrium content above 8%, resulting in the ZrO layer on top of the substrate followed by a thin Oxide and then the YZO film. Before exceeding 8% Yttrium, those features in the substrate interface are seen to a much lesser extent. The resistivity data from Matt Melfi's paper also suggested that the Zr substrates were the best of the 8% Yttrium samples, in that they had the best conductivity. This is due to the quality of the substrate interfaces of the films on Zr substrates.

The interfaces of the films on Si substrates were the most compromised from roughening. (conformal roughening) The interfaces of the films on Al2O3 substrates were sharper, but still showed roughening. The interfaces of the films on Zr substrates showed minimal roughening and a sharper overall interface to the YZO then the other substrates. The better substrate interface leads to lower resistivity in the YZO on Zr substrates.

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Appendix 1

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December 18, 2022

Seton Hall University
Thesis Archive

RE: Jeff Serfass - Master of Arts and Sciences thesis

To whom it may concern:

Please let it be known that Jeff Serfass included in his master's thesis, certain very general images and figures from Eurofins-EAG technical documentation. These images are all in the public domain and are all used with permission. Please feel free to contact me with any questions.

Sincerely,
Jeff

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